Local nonequilibrium effects in kinetic theory : The Boltzmann equation(Dissertation_全文)

AUTHOR(S):

Kim, Hyeon-Deuk

Local Nonequilibrium Effects in Kinetic Theory

The Boltzmann Equation

Kim Hyeon-Deuk

March, 2004

Local Nonequilibrium Effects in Kinetic Theory
The Boltzmann Equation

Kim Hyeon-Deuk

Kyoto University
Graduate School of Human and Environmental Studies
Sakyo-ku, Kyoto 606-8501, Japan

e-mail:kim@yuragi.jinkan.kyoto-u.ac.jp

Acknowledgments

The author would like to deeply appreciate my supervisor Prof. Hisao Hayakawa for giving me a start to study physics and a chance to specialize in kinetic theory. I am also thankful that he has made communication or discussions with me almost everyday, and always encouraged me to carry out my works. I wish to express my sincere appreciation to Prof. Shin-ichi Sasa who has made me aware of physical significance of understanding local nonequilibrium phenomena, and always made the crucial, interesting and cheerful discussions with me. I believe that this thesis would not exist if I did not meet two of them.

I am obliged to Prof. A. Santos and Prof. V. Garzó for making fresh and exciting discussions with me and giving me many interesting indications during my stay at Universidad de Extremadura in Spain. I would also like to express my sincere gratitude to Prof. H. Tasaki, Dr. Ooshida. T, Prof. A. Yoshimori, Prof. M. Sakagami, Prof. M. Fushiki, Prof. Y. Miyamoto, Prof. M. Sugiyama, Prof. M. Kuramoto, Dr. M. Sano, Dr. J. Wakou, Dr. K. Sato, Dr. K. Ichiki, Dr. M. Isobe, Dr. A. Awazu, Dr. K. Miyazaki, Prof. T. Mizuguti, Dr. T. Chawanya, Prof. S. Takesue and Prof. H. Tomita for their fruitful discussions and useful comments. I thank my colleagues, H. Kuninaka, S. Wada, T. Ayukawa, C. Urabe, T. Mitsudo and N. Yajima for giving me a nice environment for study.

I wish to express my sincere thanks to all of my family who have watched out for me and thought of me most deeply. They have always given me peace of mind, and their much of love has let me be me.

All my researches in this doctoral paper was performed in the Graduate school of Human and Environmental Studies of Kyoto University. Finally, I would like to appreciate the Japan Scholarship Foundation, Kashiyama Scholarship Foundation and Shouwa Houkoukai for supporting my student

life, and the Japan Science Society and Kim Man-Yu Scientific Foundation for supporting my researches.

Abstract

It is one of the most significant subjects in the modern statistical physics to establish the nonequilibrium statistical mechanics and the nonequilibrium thermodynamics which can describe nonequilibrium states beyond local equilibrium states. Such the nonequilibrium statistical physics has not been essentially understood yet even in simple systems such as dilute gases. The main aims of this thesis are to detect local nonequilibrium effects in microscopic kinetic theory and to examine, from the kinetic point of view, the nonequilibrium statistical mechanics and the nonequilibrium thermodynamics which do not adopt the local equilibrium hypothesis. These will serve to construct the nonlinear nonequilibrium statistical mechanics and thermodynamics whose comprehensive understanding is still lacking.

In order to achieve the goal, we have derived the explicit velocity distribution function of the steady-state Boltzmann equation for hard-core molecules to second order in a heat flux by the Chapman-Enskog method. This enables us to compare it directly with that for Maxwell molecules in order to confirm whether there exists the universal nonlinear nonequilibrium statistical mechanics from the microscopic viewpoint. In their nonlinear nonequilibrium transport phenomena, we have found qualitative differences between thermodynamical quantities of hard-core molecules and those of Maxwell molecules, and also demonstrated that the steady-state Bhatnagar-Gross-Krook(BGK) equation belongs to the same universality class as that of Maxwell molecules. The suggestion has been made that molecules which interact via other central potentials still have the qualitative differences from Maxwell molecules, and that the steady-state BGK equation does not capture the essence of such the molecules.

Owing to the derivation of the explicit nonlinear nonequilibrium velocity distribution function of the steady-state Boltzmann equation for hard-core

molecules, we become able to calculate the effect of a steady heat flux on the rate of chemical reaction based on the line-of-centers model. We have found that the second-order velocity distribution function plays an essential role for the calculation of it. This indicates the significance of the second-order coefficients in the solution of the steady-state Boltzmann equation as terms which reflect the local nonequilibrium effect. We have also compared our result with those from the steady-state BGK equation and information theory, and confirmed no qualitative differences among them.

Finally, we have examined the validity of the nonlinear nonequilibrium statistical mechanics and the nonlinear nonequilibrium thermodynamics, *i.e.* information theory and the steady state thermodynamics(SST), on the steady-state Boltzmann equation using its nonlinear nonequilibrium velocity distribution functions. We have found that information theory is completely inconsistent with the steady-state Boltzmann equation, and that, in a simple nonequilibrium steady-state system, SST conflicts with the steady-state Boltzmann equation. The physical interpretations for these results of our examinations are also proposed.

List of Publications

1. Kim H.-D. and H. Hayakawa, Chem. Phys. Lett. Vol.372 No.3-4 pp.314-319 (2003).

Contributions of Steady Heat Conduction to the Rate of Chemical Reaction

2. Kim H.-D. and H. Hayakawa, Recent Advances in Interdisciplinary Applied Physics, to be published.

Contributions of Steady Heat Conduction to the Rate of Chemical Reaction

3. Kim H.-D. and H. Hayakawa, AIP conference proceedings, to be published.

Contributions of Steady Heat Conduction to the Rate of Chemical Reaction

4. Kim H.-D. and H. Hayakawa, J. Phys. Soc. Jpn. Vol.72 No.8 pp.1904-1916 (2003).

Kinetic Theory of a Dilute Gas System under Steady Heat Conduction

5. Kim H.-D. and H. Hayakawa, J. Phys. Soc. Jpn. Vol.72 No.10 pp.2473-2476 (2003).

Test of Information Theory on the Boltzmann Equation

6. Kim H.-D. and H. Hayakawa, J. Phys. Soc. Jpn. Vol.70 No.7 pp.1954-1965 (2001).

Statistical Properties of Inelastic Lorentz Gas

Contents

1 Historical Review and Motivation **9**

1.1 Kinetic Theory 9

1.2 Chemical Reaction 15

1.3 Nonlinear Nonequilibrium Statistical Mechanics and Thermodynamics 17

1.3.1 Nonequilibrium Statistical Mechanics: Information Theory 17

1.3.2 Nonequilibrium Thermodynamics: Extended Irreversible Thermodynamics(EIT) and Steady State Thermodynamics(SST) 19

1.4 Our Motivation and Organization of This Thesis 22

2 Kinetic Theory of a Dilute Gas System under Steady Heat Conduction **25**

2.1 Method for Solving the Steady-State Boltzmann Equation . . 25

2.2 Burnett's Method 27

2.2.1 A general form of the velocity distribution function . . 27

2.2.2 The collision term Δ_{kr} 31

2.2.3 Determination of B_{kr} 32

2.3 The Chapman-Enskog Solution of the Steady-State BGK Equation to second order 40

2.4 Direct comparison of the scaled $\phi^{(2)}$ 42

2.5 Nonlinear Nonequilibrium Transport Phenomena 43

2.6 Discussion and Conclusion 45

3 Contributions of Steady Heat Conduction to the Rate of Chemical Reaction **50**

3.1 Calculation of the Rate of Chemical Reaction 50
3.2 Local Nonequilibrium Effects on the Rate of Chemical Reaction 51
3.3 Discussion and Conclusion 55

4 Examination of Information Theory and Steady State Thermodynamics(SST) on the Boltzmann Equation 58
4.1 Information Theory 58
4.2 Nonlinear Nonequilibrium Thermodynamics 60
4.2.1 Extended Irreversible Thermodynamics(EIT) 60
4.2.2 Steady State Thermodynamics(SST) 62
4.3 Examination 64
4.3.1 Test of Information Theory 64
4.3.2 Test of Steady State Thermodynamics(SST) 66
4.4 Discussion and Conclusion 69

5 Summary 73
5.1 Kinetic Theory 73
5.2 Chemical Reaction 74
5.3 Nonlinear Nonequilibrium Statistical Mechanics and Thermodynamics 75

6 Future Perspectives of Nonequilibrium Statistical Physics 77

A Calculation of Ω_{kr} 80

B Details of $F^1_{kr}(\chi)$ 82

C Calculation of $\Xi^{r,n_1,n_2,p_1,p_2}_{k,k_1,k_2}(\chi)$ 84
C.1 Introduction of $\Theta^{p_1,p_2}_{k,k_1,k_2}$ 84
C.2 Derivation of the Inductive Equation 85
C.3 Calculation of the Initial Value 87
C.4 Evaluation of $\Xi^{r,n_1,n_2,p_1,p_1}_{k,k_1,k_2}(\chi)$ 88

D Calculation of the First Order Coefficients B^{I}_{kr} 89

E Calculation of the Second Order Coefficients B^{II}_{kr} 91

F Matrix Elements **97**

F.1 $M^{r,n_1,0,0,0}_{1,1,0}$ for $1 \leq r \leq 7$ and $1 \leq n_1 \leq 7$ 97

F.2 $M^{r,n_1,0,0,0}_{0,0,0}$ for $2 \leq r \leq 6$ and $2 \leq n_1 \leq 6$, and $M^{r,n_1,n_2,0,0}_{0,1,1}$ for $2 \leq r \leq 6$, $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ 97

F.3 $M^{r,n_1,0,0,0}_{2,2,0}$ for $0 \leq r \leq 6$ and $0 \leq n_1 \leq 6$, and $M^{r,n_1,n_2,0,0}_{2,1,1}$ for $0 \leq r \leq 6$, $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ 99

Chapter 1

Historical Review and Motivation

1.1 Kinetic Theory

The kinetic theory has a long history, and numerous studies on describing behaviors of gases have been carried out analytically, numerically and experimentally.[1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21] The behaviors of gases in nonequilibrium states have received considerable attention from the standpoint of understanding the characteristics of nonequilibrium phenomena. The kinetic theory has contributed not only to the understanding of nonequilibrium transport phenomena in gases but also to the development of general nonequilibrium statistical physics.

It is well accepted that the Boltzmann equation is one of the most reliable kinetic models for describing nonequilibrium phenomena in dilute gases. Many text books on the Boltzmann equation show the fact that the Boltzmann equation has attracted much interest among researchers of kinetic phenomena.[1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21] The Boltzmann equation without external forces has the form,

$$\frac{\partial f_1}{\partial t} + \mathbf{v}_1 \cdot \nabla f_1 = J(f_1, f_2), \tag{1.1}$$

where the collision integral $J(f_1, f_2)$ is expressed as

$$J(f_1, f_2) \equiv \int\int\int (f_1' f_2' - f_1 f_2) g b \mathrm{d}b \mathrm{d}\epsilon \mathrm{d}\mathbf{v}_2, \tag{1.2}$$

with $f_1' = f(\mathbf{r}, \mathbf{v}_1')$ and $f_2' = f(\mathbf{r}, \mathbf{v}_2')$: $\mathbf{v}_1'$ and $\mathbf{v}_2'$ are postcollisional velocities of $\mathbf{v}_1$ and $\mathbf{v}_2$, respectively. The relative velocity of two molecules before and after an interaction has the same magnitude $g = |\mathbf{v}_1 - \mathbf{v}_2|$; the angle between the directions of the relative velocity before and after the interaction is represented by χ. The relative position of the two molecules is represented by b, called the impact parameter, and ϵ represents the orientation of the plane in which $\mathbf{g}$ and $\mathbf{g}' = \mathbf{v}_1' - \mathbf{v}_2'$ belong. Note that χ can be expressed as a function of b for a central force.

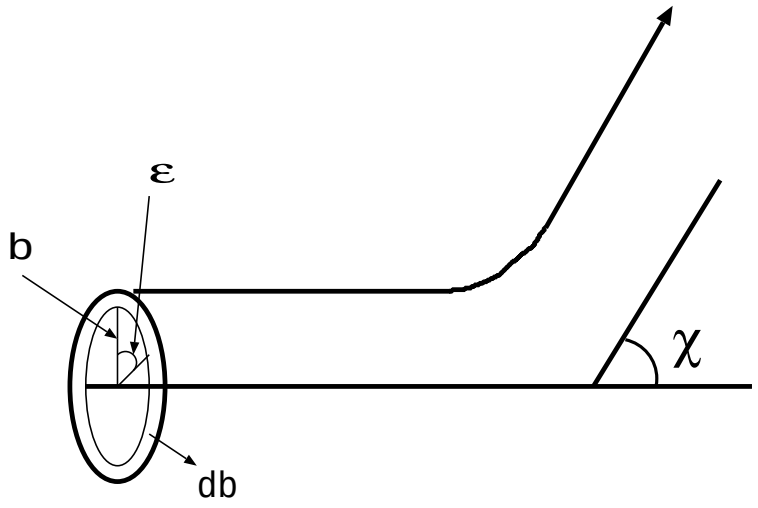

Figure 1.1: Schematic description of an interaction.

The impact parameter b depends on the kind of interactions between molecules, and one should specify the intermolecular interactions so as to explicitly determine the impact parameter b in the collision term of the Boltzmann equation. A number of studies on the Boltzmann equation have been based on two representative models of molecules: hard-core molecules and Maxwell molecules[22, 23, 24]. The former interacts via an impulsive force at the moment of collisions between molecules, so that it is not needed to consider any long range forces between the collisions. For hard-core molecules, the impact parameter becomes $b = d\cos\frac{\chi}{2}$ with the hard-core molecular diameter d, so that the collision differential cross section is given by

$$b\mathrm{d}b = -\frac{d^2}{2}\cos\frac{\chi}{2}\sin\frac{\chi}{2}d\chi, \tag{1.3}$$

Maxwell molecules interact via a force which is inversely proportional to the fifth power of the distance r, that is, Maxwell molecules interact via a central potential proportional to r^{-4}. For Maxwell molecules, it is given by the relation

$$b\mathrm{d}b = \frac{1}{g}H(\chi)\mathrm{d}\chi, \tag{1.4}$$

where $H(\chi)$ is a function of χ.[6, 22, 23, 24] This leads to the characteristic property of Maxwell molecules that the collision frequency is independent of relative speed of colliding molecules. It is well known that, because of this simplicity, calculations involving the Boltzmann equation for Maxwell molecules become much easier than those for hard-core molecules.[1, 22, 23, 24, 25, 26, 27, 28]

The Boltzmann equation is based on the physical assumption of molecular chaos, which means that all the correlations after intermolecular collisions attenuate exponentially with time, and that all the molecules have no memory of their past collisions, which leads to the time-irreversibility of the Boltzmann equation as is exhibited in the H-theorem.[29] Some numerical experiments have shown that this assumption is valid so long as a clear scale separation $d \ll l$ holds, where d is a diameter of molecules and $l \sim 1/nd^2$ denotes the mean free path of gases.[30, 31, 32] Theoretically, it is believed that the Boltzmann equation is valid for the Boltzmann-Grad limit, $nd^3 \ll 1$ with the finite mean free path l. In fact, the Boltzmann equation can be derived from the Bogolyubov-Born-Green-Kirkwood-Yvons(BBGKY) equations for one-particle velocity distribution function by neglecting higher order collision interactions which corresponds to finite density contributions.[33] The BBGKY equation is deduced from the N-body Liouville equation by integrating by phase space variables of $N-1$ molecules with an assumption that the $N-1$ molecules can not be distinguished from each other.[33] Another condition which lets the Boltzmann equation hold will be discussed and explicitly indicated in Sec.2.6. It also makes the Boltzmann equation reliable that macroscopic equations such as the Navier-Stokes equation can be derived from the Boltzmann equation by perturbation methods which will be mentioned in the paragraph after the next. The linear transport coefficients from the Boltzmann equation are verified to be consistent with experimental results. Therefore, it can be concluded that the linear transport phenomena in plain monatomic gases are well established and understood by the Boltz-

mann equation. The hierarchy mentioned above is summarized in Table 1.1.

Table 1.1: Hierarchy of the Boltzmann equation

STAGE	Dynamic	Kinetic	Hydrodynamic
EQUATION	**Liouville Eq.**	**Boltzmann Eq.**	**Navier-Stokes Eq.**
LENGTH	Molecule's Size d	Mean Free Path l	Thermodynamic Change L
VARIABLES	Density Function	Distribution Function	Thermodynamic Quantity
REVERSIBILITY	Reversible	Irreversible	Irreversible

For finite density gas systems where the Boltzmann equation does not give any correct descriptions, even the linear transport coefficients cannot be exactly derived, though there is a phenomenological theory, Enskog theory, whose results of the linear transport coefficients agree well with those of numerical experiments.[1] For finite density gases, one can only calculate some correlation functions using ring kinetic theory, so that the linear transport coefficients can be obtained only indirectly from the Green-Kubo formula. The previous researches have reported the existence of long-range and long-time correlations in nonequilibrium phenomena of dense gases.[29, 31, 34, 35, 36] For example, they have demonstrated the long-time tail in the velocity correlation functions, $t^{-3/2}$ for three dimension and t^{-1} for two dimension. The latter leads to the divergence of the linear transport coefficients in two dimension, which has been confirmed by numerical experiments.[37] The effects of long-range and long-time correlations can be supported by the fact that hydrodynamic frequencies for sound, shear and heat modes have a nonanalytic dependence on wave number. There have been also some investigations of the divergence of the nonlinear transport coefficients even in a three dimension, which will be discussed in Sec.2.6.[38, 39, 40]

In the early stage of studies on the kinetic theory, great effort has been paid for solving kinetic model equations such as the Boltzmann equation and deriving nonequilibrium distribution functions and macroscopic nonequilibrium transport equations in terms of microscopic molecular quantities. As will be mentioned in Sec.1.3, these attempts were strongly related to the development of general nonequilibrium statistical physics such as linear nonequilibrium thermodynamics, Onsager's reciprocal theorem and the linear

response theory.[29, 41, 42, 43, 44] In order to derive the velocity distribution functions of dilute gases in a nonequilibrium state, various methods which give normal solutions of the Boltzmann equation have been presented.[1, 2, 3, 4, 5, 6, 7, 8, 9, 13, 14, 15, 16, 17, 24, 25, 26, 27, 28, 45, 46, 47, 48, 49, 50] The first analysis of the Boltzmann equation was performed by Hilbert.[7, 51, 52] He obtained the formal solution of the Boltzmann equation by expanding the velocity distribution function and also the macroscopic quantities such as density, mean flow and temperature. However, the Navier-Stokes equation never appears in the Hilbert method where the macroscopic quantities are expanded and one have to sum up them to obtain the correct hydrodynamic quantities. For this reason, Enskog and Chapman independently modified the Hilbert method and developed it into the Chapman-Enskog method where only the velocity distribution function is expanded.[1, 8, 9, 49, 50] The Chapman-Enskog method is adopted through this thesis, and its details will be explained in the next chapter. There is also another developed method to obtain the normal solution of the Boltzmann equation called the Grad method.[45, 46, 47, 48] In this method, coefficients which appear in the formally expanded velocity distribution function are determined by a moment method, so that the number of the moments corresponding to the coefficients must be specified artificially before one derive the solution. It is well known that this method and the Chapman-Enskog method gives identical results in linear transport equations. However, including nonlinear transport phenomena, the relation between these two methods is not made clear yet. For the linearized Boltzmann equation, there is an eigenvalue method to calculate the linear transport coefficients which gives the same results as the Chapman-Enskog method for the Boltzmann equation, except that density and temperature appearing in the linear transport coefficients are absolute equilibrium ones, that is, they are constant.[3] In all the perturbation methods mentioned above, the small expansion parameter will turn out the Knudsen number $K = l/L$, which means that the mean free path of molecules l should be much less than the characteristic length L for changes in the macroscopic variables. The other perturbation method, the S-expansion method, was proposed by Sone, where he focused on the gas fluid dynamics of the finite Reynolds number $Re = U^*L^*n/\eta$ with characteristic speed U^*, characteristic length L^*, density n and viscosity η. In this case, the Mach number $Ma = U^*/U_{\text{sound}} (\propto ReK)$ with a sound speed U_{sound} has the same order of the Knudsen number. Sone assumes a deviation of the nonequilibrium

solution from the *uniform* equilibrium one is of K, which leads to results that the leading-order solutions of the S-expansion method become not the Euler equation but the Navier-Stokes equation, and that its higher-order solutions become compressible hydrodynamic equations reflecting effects of Ma. The S-expansion method expands not only the velocity distribution function but also the macroscopic quantities, so that it corresponds to the case where the solutions of the Hilbert method at the leading order, from which the Euler equation is derived, are uniform and at rest.[7]

It had been believed that Burnett determined the complete second-order solution of the Boltzmann equation by the Chapman-Enskog method.[1, 25] Physical importance of the second-order coefficients has been also demonstrated for descriptions of shock wave profiles and sound propagation phenomena.[10, 53, 54, 55, 56, 57, 58] However, we have realized that Burnett's solution is not complete.[25, 59] Though there are various studies on the transport coefficients of the Boltzmann equation to second order[1, 3, 4, 11, 47, 48] or even to third order[58], we have found that nobody has derived the explicit velocity distribution function of the Boltzmann equation for hard-core molecules to second order.[59] This is a result of mathematical difficulties, as was indicated by Fort and Cukrowski[60]. For Maxwell molecules, because of its simplicity, Schamberg[26] has derived the precise velocity distribution function of the Boltzmann equation to second order by the Chapman-Enskog method, while Shavaliev[27] has derived it implicitly by the moment method. Heat transfer for Maxwell molecules in a steady state was also reported in ref.[28].

Other kinetic models besides the Boltzmann equation, such as the linearized Boltzmann equation[5, 61, 3] and the Bhatnagar-Gross-Krook (BGK) equation[62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73], have also been proposed to avoid mathematical difficulties in dealing with the collision term of the Boltzmann equation. It has been believed that results of those kinetic models approximately agree with those of the Boltzmann equation, though they are accepted as quantitatively different ones from the Boltzmann equation: *e.g.* the Prandtl number, $\eta C_p/\lambda$ with C_p specific heat at constant pressure and λ thermal conductivity, is $2/3$ for the Boltzmann equation, while it is 1 for the BGK equation.[7, 64, 65]

The BGK equation is written as

$$\frac{\partial f_1}{\partial t} + \mathbf{v}_1 \cdot \nabla f_1 = \frac{f_{LE} - f_1}{\tau}. \tag{1.5}$$

τ represents a characteristic time of relaxation of f_1 to a local equilibrium velocity distribution function f_{LE}. The relaxation time τ depends not on velocity of molecules but on its position $\mathbf{r}$ through the macroscopic quantities such as the density and the temperature. It has been felt that characteristics of molecules, such as hard-core molecules and Maxwell molecules, can be absorbed into the relaxation time τ. The BGK equation retains important properties of the Boltzmann equation, such as the conservation laws and the H-theorem. Its linear version can be *derived* from the linearized Boltzmann equation.[3, 5] However, it is not clear yet whether the BGK equation (2.42) really brings a decisive simplification in deal with nonequilibrium gas behaviors. The most important advantage of the BGK equation is that it can be easily solved. Lebowitz proposed a BGK-like model and confirmed that its first-order velocity distribution function is identical with that for the BGK equation[63], and Trilling has discussed the second-order velocity distribution function for the BGK equation although he did not employ the Chapman-Enskog solution method.[74] There are several studies of the second-order transport coefficients using the BGK equation.[64, 75] The most valuable contribution concerning the solution of the BGK equation has been made by Santos and his coworkers.[66, 67, 68, 69, 70, 71, 72, 73] They have solved the steady-state BGK equation exactly and compared its exact solution with the perturbation solution by the Chapman-Enskog method deduced to arbitrary order.[66, 67, 68, 69, 70] They have concluded that the Chapman-Enskog solution is asymptotically correct, although the series of the Chapman-Enskog expansion diverge.

1.2 Chemical Reaction

Following its success and usefulness, the Boltzmann equation is widely used in order to describe various dilute gas-phase transport phenomena such as granular gases[76, 77, 78, 79, 80, 81, 82, 83], plasma gases[19, 20], polyatomic gases[21, 84, 85], relativistic gases[86] and chemically reacting gases.

Chemical reactions in gases have been studied with the aid of gas collision theory. In the early stage of a chemical reaction between monatomic gas molecules:

$$A + A \rightarrow \text{products}, \tag{1.6}$$

the rate of chemical reaction may not be affected by the existence of prod-

ucts and the reverse reaction can be neglected.[87] From the viewpoint of kinetic collision theory[1, 3, 13, 18], the rate of chemical reaction (1.6) can be described as

$$R = \int d\mathbf{v} \int d\mathbf{v}_1 \int d\mathbf{\Omega} \int f f_1 g \sigma(g), \tag{1.7}$$

where $\mathbf{\Omega}$ denotes the solid angle. Though various models have been suggested as the differential cross-section of chemical reaction $\sigma(g)$[88, 89, 90, 91, 92], the line-of-centers model proposed by Present has been accepted as a standard model to describe the chemical reaction in gases.[18, 60, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106]The line-of-centers model contains

$$\sigma(g) = \begin{cases} 0 & g < \sqrt{\frac{4E^*}{m}} \\ \frac{d^2}{4}\left(1 - \frac{4E^*}{mg^2}\right) & g \geq \sqrt{\frac{4E^*}{m}} \end{cases}, \tag{1.8}$$

with m mass of molecules and E^* the threshold energy of a chemical reaction. This model can be derived explicitly using a collision law of hard-core molecules, and the diameter of hard-core molecules d is regarded as a distance between centers of monatomic molecules at contact.[18, 92, 93] The line-of-centers model contains an incoherence that , since some of activated complex decompose into the initial reactants rather than into the products of the reaction, the cross-section for reaction will be smaller than that for complex formation. However, the two cross-sections will usually differ by a factor of the order of unity, this factor may be absorbed in the uncertain reaction diameter d. Actually, in equilibrium states, an experimental result including the temperature dependency can be fitted by the results from the line-of-centers model with a relevant value of d.[18, 89] The line-of-centers model can also reproduce experimental results of effects of density and temperature decreases of reacting gases on chemical reaction rate.[90]

Several attempts have been conducted on effects of density and temperature change of reactants on the rate of chemical reaction[88, 90, 91, 92, 94, 95, 96, 99, 103, 104, 105, 106] and effects of chemical reactions on the nonequilibrium transport coefficients [97, 98]. Furthermore, under nonequilibrium situations such as gases under heat conduction and shear flows, their pure nonequilibrium contributions on the rate of chemical reaction have attracted much attention.[60, 100, 101, 102, 107, 108, 109] Since the nonequilibrium

correction terms of the rate of chemical reaction are quadratic functions of nonequilibrium fluxes, to derive the pure effect of nonequilibrium fluxes on it based on the line-of-centers model, we need the explicit velocity distribution function of the Boltzmann equation for hard-sphere molecules to second order in nonequilibrium fluxes.[102, 108, 109] Therefore, none has succeeded to obtain the nonequilibrium effect of the line-of-centers model except for Fort and Cukrowski who adopted information theory[110, 111, 112] as the nonequilibrium velocity distribution function to second order.[60, 100]

1.3 Nonlinear Nonequilibrium Statistical Mechanics and Thermodynamics

It is one of the most significant subjects in the modern statistical physics to construct the nonequilibrium statistical mechanics and the nonequilibrium thermodynamics for strongly nonequilibrium states beyond local equilibrium states. We call such the nonequilibrium state as the *local nonequilibrium state*. In this section, we have summarized the previous attempts.

1.3.1 Nonequilibrium Statistical Mechanics: Information Theory

The maximum entropy formalism based on information theoretical approach[113, 114] for statistical mechanics is suggested by Jaynes.[115] Zubarev[33, 116] has developed nonequilibrium statistical mechanics and obtained the general form of a nonequilibrium velocity distribution function with the aid of the maximum entropy principle. Thereafter the nonequilibrium velocity distribution function to first order has been derived by expanding the Zubarev form for the nonequilibrium velocity distribution function under some constraints.[117]

Jou and his coworkers have derived the nonequilibrium velocity distribution function to second order by expanding the Zubarev form for the nonequilibrium velocity distribution function to second order under the some constraints, which is called information theory.[110, 111, 112] Its details will be explained in Sec.4.1. Information theory has attracted interest in the development of a general framework for nonlinear nonequilibrium statistical

mechanics which can describe the *local nonequilibrium state*. Even a text book on information theory has been published.[110] Jou *et al.* have applied the nonequilibrium velocity distribution function from information theory to nonequilibrium systems, and made some predictions based on information theory in the systems. For example, in dilute gas systems under nonequilibrium fluxes, an anisotropic pressure and a nonequilibrium temperature which is not identical with kinetic temperature have been predicted.[118, 119, 120] They have presented some experiments on an anisotropic Doppler relaxation and change of sound speed owing to these nonequilibrium thermodynamic quantities.[121] The anisotropic pressure is also calculated for ultra-relativistic gas and non-viscous gas in nonequilibrium states: the former is required for astrophysical plasma where heat fluxes can be extremely high.[119, 122] Furthermore, Jou *et al.* have also considered nonequilibrium corrections to radiation intensity and the Planck distribution function of radiative systems using information theory[123, 124, 125, 126, 127], and a more explicit radiative equation of Maxwell-Cattaneo type than the usual radiative transfer equation has been obtained.[127] There are also several applications of information theory to chemically reacting gases, as was mentioned in Sec.1.2.[60, 100]

Nettleton claimed that information theory provides a statistical mechanical basis of irreversible processes and of extended thermodynamics which is consistent with the laws of thermodynamics[107, 128], although he gave information theory a criticism and developed the maximum entropy formalism.[102, 108, 129] However, in the actual applications, it is not easy to examine information theory. We have to find qualitative differences between information theory and the microscopic theories in the applications so as to demonstrate the invalidity of information theory as a universal nonequilibrium statistical mechanics. In fact, as will be reported in Sec.3.2, though we have compared the effect of steady heat flux on the rate of chemical reaction calculated from information theory with those which we have calculated from kinetic theories, we have found no qualitative differences among them.[130] To our knowledge, there are no reports which conclude that information theory is not an appropriate theory to describe nonequilibrium phenomena. As was indicated in refs.[60] and [112], more examinations of information theory should be carried out from the microscopic viewpoint so as to confirm whether there exists universality in nonlinear nonequilibrium statistical mechanics.

1.3.2 Nonequilibrium Thermodynamics: Extended Irreversible Thermodynamics(EIT) and Steady State Thermodynamics(SST)

The linear nonequilibrium thermodynamics called thermodynamics of irreversible processes(TIP) has been developed, based on the local equilibrium hypothesis which requires that a nonequilibrium state can be regarded as locally equilibrium, and that the nonequilibrium system can be described by the local equilibrium thermodynamic quantities. This requirement is valid only when nonequilibrium fluxes are not so large. In TIP, the Gibbs equation is extended by making all the thermodynamic quantities in the equation depend on space and time. TIP requires the second law of thermodynamics, that is, the local entropy production is always positive in any nonequilibrium irreversible processes, which leads to restrictions on the linear transport equations.[41, 42, 43, 107, 131, 132] There are also important theorems to describe irreversible processes which have contributed to construct the linear nonequilibrium thermodynamics: (i) the theory of minimum entropy production by Prigogine which characterizes nonequilibrium steady states, (ii) the principle of the least dissipation of energy by Onsager which gives a proportional relation between the time-evolution of hydrodynamic fluctuations and a thermal force towards equilibrium, and (iii) Onsager's reciprocal theorem which gives a symmetrical relation between the coefficients of the proportionality corresponding to the linear transport coefficients. These nonequilibrium theories are inspired and confirmed by results of hydrodynamic transport equations from the kinetic theories. It can be stated that the linear nonequilibrium statistical physics has been almost established.

On the other hand, nonlinear nonequilibrium statistical physics has not been essentially understood yet. There are even *some* nonlinear nonequilibrium thermodynamics which are constructed with a *local nonequilibrium hypothesis*. The *local nonequilibrium hypothesis* means that nonequilibrium gradients and fluxes in a nonequilibrium system are too large to be neglected even locally, so that, in order to describe such the nonequilibrium state, one must adopt the nonequilibrium fluxes as new thermodynamic variables.

Actually, in the extended thermodynamics(ET) which is the first nonlinear nonequilibrium thermodynamics, the nonequilibrium fluxes appear in the Gibbs equation and also in the entropy flux as extensive thermodynamical

variables.[133, 134, 135] ET have required that the nonequilibrium entropy production is always positive, and made restrictions on continuum equations of the thermodynamic quantities, although the continuum equations cannot be fully determined by them and some results from other microscopic theories are needed. ET has been tested by comparing the continuum equations from ET with those from gas fluids. [122, 136]

Extended irreversible thermodynamics(EIT) proposed by Jou *et al.* is also the nonlinear nonequilibrium thermodynamics based on the *local nonequilibrium hypothesis*.[110, 111, 112] EIT extends the Gibbs equation not only by making all the thermodynamic quantities in the equation depend on space and time, but also by treating the nonequilibrium fluxes as extensive thermodynamic variables. Using a relaxation law of the nonequilibrium fluxes such as Maxwell-Cattaneo's law, the nonequilibrium entropy is determined so as to make the production of the nonequilibrium entropy always positive. (see Sec.4.2) However, the expression still contains the relaxation time and the thermal conductivity which depends on the characteristics of microscopic materials, and the relation between two of them should be calculated from other microscopic theories. Jou *et al.* have claimed that EIT is in harmony with information theory: the nonequilibrium entropy and the nonequilibrium temperature determined in EIT is identical with those calculated from information theory. EIT is itself applied to nonequilibrium systems such as chemically reacting gas.[137] The more details of EIT will be explained in Sec.4.2.

There is another nonlinear nonequilibrium thermodynamics based on the *local nonequilibrium hypothesis*, steady-state thermodynamics(SST).[138] Sasa and Tasaki have recently suggested SST, inspired by Oono and Paniconi.[139] SST has obtained not the Gibbs equation but the Euler equation by assuming an additive thermodynamic potential where the nonequilibrium flux such as a heat flux is treated as an intensive thermodynamic variable. SST has considered a nonequilibrium system in which an equilibrium cell and the nonequilibrium cell under steady heat conduction connected by a porous wall(see Fig.2 in ref.[138]), and the nonequilibrium chemical potential or the nonequilibrium pressure in the nonequilibrium cell obtained from the thermodynamic potential are defined operationally by the corresponding equilibrium values in the equilibrium cell. This enable SST to be self-contained and make some nontrivial predictions without any other microscopic theories. The details of SST will be explained in Sec.4.2.

We summarize the three nonlinear nonequilibrium thermodynamics mentioned in this section by comparing them from others in Table 1.2. One

Table 1.2: Comparison of the nonlinear nonequilibrium thermodynamics. Note that J denotes a nonequilibrium flux such as a heat flux.

	ET	**EIT**	**SST**
Degree of Nonequilibrium	J^2	J^2	J^2
Nonequilibrium Flux	Extensive	Extensive	Intensive
Thermodynamic Potential	Entropy	Entropy	Free Energy
Additivity	Additive	Additive	Additive
Extended Equation	Gibbs Eq.	Gibbs Eq.	Euler Eq.
Thermodynamic Structure	Not Self-Contained	Not Self-Contained	Self-Contained

can find that SST is quite different from ET and EIT as is shown in Table 1.2. ET and EIT are not self-contained, so that ET requires the undetermined transport coefficients to be calculated from other microscopic theories, and EIT needs a relaxation law of the nonequilibrium fluxes such as Maxwell-Cattaneo's law, and the relation between the relaxation time and the thermal conductivity calculated from other microscopic theories. Contrary to these two nonlinear nonequilibrium thermodynamics, SST does not require any other microscopic theories because SST is self-contained. However, it includes another undetermined problem, that is, a way to connect the nonequilibrium cell with the equilibrium one.

The nonlinear nonequilibrium thermodynamics mentioned above have some similarities: (1) all of them assume the additivity of thermodynamic quantities, and (2) all of them focus on second-order effects of the nonequilibrium fluxes as local nonequilibrium effects. The latter is related to a stability of the thermodynamic structure: its thermodynamics potential function should become a quadratic function of the nonequilibrium fluxes in order that the potential has a maximum at zero flux, and that a thermodynamic force which drives a nonequilibrium system towards the state of equilibrium is proportional to the nonequilibrium flux.[44] Actually, in the nonequilibrium entropy, any nonequilibrium corrections to the local equilibrium entropy should appear to second order of a nonequilibrium flux as will be discussed

in Sec.4.4. Therefore, we also focus on the second-order solutions of microscopic kinetic equations such as the steady-state Boltzmann equation in this thesis, as will be mentioned in the next section.

1.4 Our Motivation and Organization of This Thesis

The main aims of this thesis are to detect local nonequilibrium effects in the microscopic kinetic theory and to examine the nonequilibrium statistical mechanics and the nonequilibrium thermodynamics based on the *local nonequilibrium hypothesis*. These will serve to construct the possible nonlinear nonequilibrium statistical mechanics and thermodynamics a comprehensive understanding of which is still lacking.

In order to achieve the goals, we have derived the explicit velocity distribution function of the steady-state Boltzmann equation for hard-core molecules to second order in a temperature gradient by the Chapman-Enskog method. This is one of our main results in this thesis. We believe that the second-order solution which produces nonlinear nonequilibrium transport phenomena reflects the local nonequilibrium effect. The fact mentioned in the end of the previous section indicates the significance of the second-order coefficients as terms which reflect the local nonequilibrium effect. Actually, physical importance of the second-order coefficients has been demonstrated for descriptions of some phenomena such as shock wave profiles[53, 54, 55, 56, 57] and astrophysical plasma[119, 122] where local nonequilibrium effects appear. In addition, there exists a need to confirm the existence of universal nonlinear nonequilibrium statistical mechanics from the microscopic viewpoint, so that it is physically important to derive the explicit velocity distribution function of the steady-state Boltzmann equation for hard-core molecules to second order and compare it directly with that for Maxwell molecules.[60]

In terms of the kinetic theory, it is interesting, in the nonlinear nonequilibrium transport phenomena, to inspect any physical difference between two representative models of molecules, hard-core molecules and Maxwell molecules. This is because no qualitative difference appears in the nonequilibrium thermodynamic quantities of the linear transport phenomena in single component gases, although, for two component gases, Maxwell molecules

have significant difference from other kinds of molecules that its thermal diffusion ratio becomes zero.[1] We also discuss the relation between the steady-state Boltzmann equation and the steady-state BGK equation which has not been fully understood yet. Additionally, the derivation of the explicit second-order solution by the Chapman-Enskog method will contribute to an understanding of the relation between the Chapman-Enskog method and the Grad method by the direct comparison of the solution by the Chapman-Enskog method with that by the Grad method.

The derivation of the explicit velocity distribution function of the steady-state Boltzmann equation for hard-core molecules to second order has other physical significance. It has been required for calculating a nonequilibrium effect on the rate of chemical reaction, because the nonequilibrium effect on the rate of chemical reaction does not appear to first order and it cannot be calculated by any moment methods.[60, 130] We believe that this second-order deviation from the equilibrium rate of chemical reaction also represents the local nonequilibrium effects. We apply our explicit nonequilibrium velocity distribution function to the calculation of the rate of chemical reaction in the line-of-centers model under steady heat conduction.

The organization of this thesis is as follows. In Chapter 2, we will introduce the Chapman-Enskog method to solve the steady state Boltzmann equation in Sec.2.1, and we will derive the explicit form of the velocity distribution function of the steady-state Boltzmann equation for hard-core molecules to second order in the temperature gradient in Sec.2.2. The result for the first-order coefficients is presented in eq.(2.32), and those for the second-order coefficients are expressed in eqs.(2.36) and (2.37). The second-order velocity distribution function of the steady-state Boltzmann equation for hard-core molecules is shown explicitly in eq.(2.40) and graphically in Fig.2.3, and compared directly with that for Maxwell molecules (2.41) in Fig.2.4. The corresponding solution for the steady-state BGK equation is introduced in Sec.2.4. In Sec. 2.5, we will apply the velocity distribution function to second order for hard-core molecules (2.40) and those for Maxwell molecules (2.41) and the steady-state BGK equation to a nonequilibrium steady-state system under steady heat conduction and calculate some thermodynamical quantities. We stress the existence of the qualitative differences among hard-core molecules, Maxwell molecules and the steady-state BGK equation in the pressure tensor (2.50) and the kinetic temperature (2.52). Our discussion is given in Sec.2.6.

In Chapter 3, we derive the local nonequilibrium effects on rate of chemical reaction introduced in eq.(1.7). We explain how to calculate the effect of steady heat flux on the rate of chemical reaction in Sec.3.1. The results are summarized in Sec.3.2, and the discussions are given in Sec.3.3.

In Chapter 4, we examine information theory and SST from a kinetic view point: we examine them by using the nonequilibrium velocity distribution functions to second order derived or introduced in Sec.2.2. We give more explanations of information theory and SST in Secs.4.1 and 4.2, respectively. They are tested in Secs.4.3.1 and 4.3.2. We will discuss about the universal nonequilibrium statistical mechanics and the nonlinear nonequilibrium thermodynamics in Sec.4.4.

In the end of this thesis, we summarize this thesis as general discussion and conclusion in Chapter 5, and give our future perspectives of nonequilibrium statistical physics in Chapter 6.

Chapter 2

Kinetic Theory of a Dilute Gas System under Steady Heat Conduction

2.1 Method for Solving the Steady-State Boltzmann Equation

Let us introduce the Chapman-Enskog method to solve the steady-state Boltzmann equation in this section. Assume that we have a system of dilute gases in a steady state, with velocity distribution function $f_1 = f(\mathbf{r}, \mathbf{v}_1)$. The appropriate steady-state Boltzmann equation is

$$\mathbf{v}_1 \cdot \nabla f_1 = J(f_1, f_2). \tag{2.1}$$

The details of the notations have been already introduced in Sec.1.1.

Suppose that the velocity distribution function f_1 can be expanded as:

$$f_1 = f_1^{(0)} + f_1^{(1)} + f_1^{(2)} + \cdots = f_1^{(0)}(1 + \phi_1^{(1)} + \phi_1^{(2)} + \cdots). \tag{2.2}$$

$f_1^{(0)}$ is the local Maxwellian distribution function, written as

$$f_1^{(0)} = n(\mathbf{r}) \left(\frac{m}{2\pi\kappa T(\mathbf{r})} \right)^{\frac{3}{2}} \exp\left[-\frac{m\mathbf{v}_1^2}{2\kappa T(\mathbf{r})} \right], \tag{2.3}$$

with m mass of the molecules and κ the Boltzmann constant. $n(\mathbf{r})$ and $T(\mathbf{r})$ will be identified later as the density and the temperature at position $\mathbf{r}$, respectively. Substituting eq.(2.2) into the steady-state Boltzmann equation (2.1), we arrive at the following set of equations which we will solve completely in this thesis:

$$L[f_1^{(0)}]\phi_1^{(1)} = \mathbf{v}_1 \cdot \nabla f_1^{(0)}, \tag{2.4}$$

to first order and

$$L[f_1^{(0)}]\phi_1^{(2)} = \mathbf{v}_1 \cdot \nabla f_1^{(1)} - J(f_1^{(1)}, f_2^{(1)}), \tag{2.5}$$

to second order. The linear integral operator $L[f_1^{(0)}]$ is defined as

$$L[f_1^{(0)}]X_1 \equiv \int\int\int f_1^{(0)} f_2^{(0)} (X_1' - X_1 + X_2' - X_2) g b \mathrm{d}b \mathrm{d}\epsilon \mathrm{d}\mathbf{v}_2. \tag{2.6}$$

The solubility conditions of the integral equation (2.4) are given by

$$\int \Phi_\mathrm{i} \mathbf{v}_1 \cdot \nabla f_1^{(0)} \mathrm{d}\mathbf{v}_1 = 0, \tag{2.7}$$

where Φ_i is one of the collisional invariants:

$$\Phi_1 = 1, \quad \Phi_2 = m\mathbf{v}_1, \quad \Phi_3 = \frac{1}{2} m \mathbf{v}_1^2. \tag{2.8}$$

Substituting eq.(2.3) into the solubility conditions (2.7), it is seen that $n\kappa T$ is uniform in the steady state. We use this result in our calculation. Similarly, the solubility conditions of the integral equation (2.5) are given by

$$\int \Phi_\mathrm{i} \mathbf{v}_1 \cdot \nabla f_1^{(1)} \mathrm{d}\mathbf{v}_1 = 0. \tag{2.9}$$

To construct solutions of the integral equations (2.4) and (2.5) definite, five further conditions must be specified; we identify the density:

$$n(\mathbf{r}) \equiv \int f_1 \mathrm{d}\mathbf{v}_1 = \int f_1^{(0)} \mathrm{d}\mathbf{v}_1, \tag{2.10}$$

the temperature:

$$\frac{3n(\mathbf{r})\kappa T(\mathbf{r})}{2} \equiv \int \frac{m\mathbf{v}_1^2}{2} f_1 \mathrm{d}\mathbf{v}_1 = \int \frac{m\mathbf{v}_1^2}{2} f_1^{(0)} \mathrm{d}\mathbf{v}_1, \tag{2.11}$$

and the mean flow:

$$\mathbf{C}_0 \equiv \int m\mathbf{v}_1 f_1 \mathrm{d}\mathbf{v}_1 = \int m\mathbf{v}_1 f_1^{(0)} \mathrm{d}\mathbf{v}_1. \tag{2.12}$$

Here we assume that no mean flow, i.e. $\mathbf{C}_0 = 0$, exists in the system. The introduction of these conditions distinguishes the Chapman-Enskog adopted here from the Hilbert method in which the conserved quantities are also expanded.[3] We assert that conditions (2.10), (2.11) and (2.12) do not affect all our results in this thesis. It should be noted that, to solve the integral equations (2.4) and (2.5), we should consider only the case in which the right-hand sides of eqs.(2.4) and (2.5) are not zero: if the right-hand sides of eqs.(2.4) and (2.5) are zero, the integral equations (2.4) and (2.5) become homogeneous equations which do not have any particular solutions.[3]

2.2 Burnett's Method

At the beginning of this section, we show the algorithm of our calculation to derive the explicit form of the velocity distribution function of the steady-state Boltzmann equation for hard-core molecules to second order in a temperature gradient. The flow chart in Fig.2.1 schematically shows all the calculation in this chapter.

2.2.1 A general form of the velocity distribution function

To solve the integral equations (2.4) and (2.5), Burnett[25] assumed a general form of the velocity distribution function:

$$\begin{aligned} f_1 &= f_1^{(0)} \left[\sum_{r=0}^{\infty} r!\Gamma(r+\frac{3}{2}) B_{0r} S_{\frac{1}{2}}^r(\mathbf{c}_1^2) \right. \\ &\quad \left. + \sum_{k=1}^{\infty} \left(\frac{m}{2\kappa T} \right)^{\frac{k}{2}} \sum_{r=0}^{\infty} r!\Gamma(k+r+\frac{3}{2}) Y_{kr}(\mathbf{c}_1) S_{k+\frac{1}{2}}^r(\mathbf{c}_1^2) \right]. \end{aligned} \tag{2.13}$$

Here $\mathbf{c}_1 \equiv (m/2\kappa T)^{1/2}\mathbf{v}_1$ is the scaled velocity and $\Gamma(X)$ represents the Gamma function. $S_k^p(X)$ is a Sonine polynomial, defined by

$$(1-\omega)^{-k-1} e^{-\frac{X\omega}{1-\omega}} = \sum_{p=0}^{\infty} \Gamma(p+k+1) S_k^p(X) \omega^p. \tag{2.14}$$

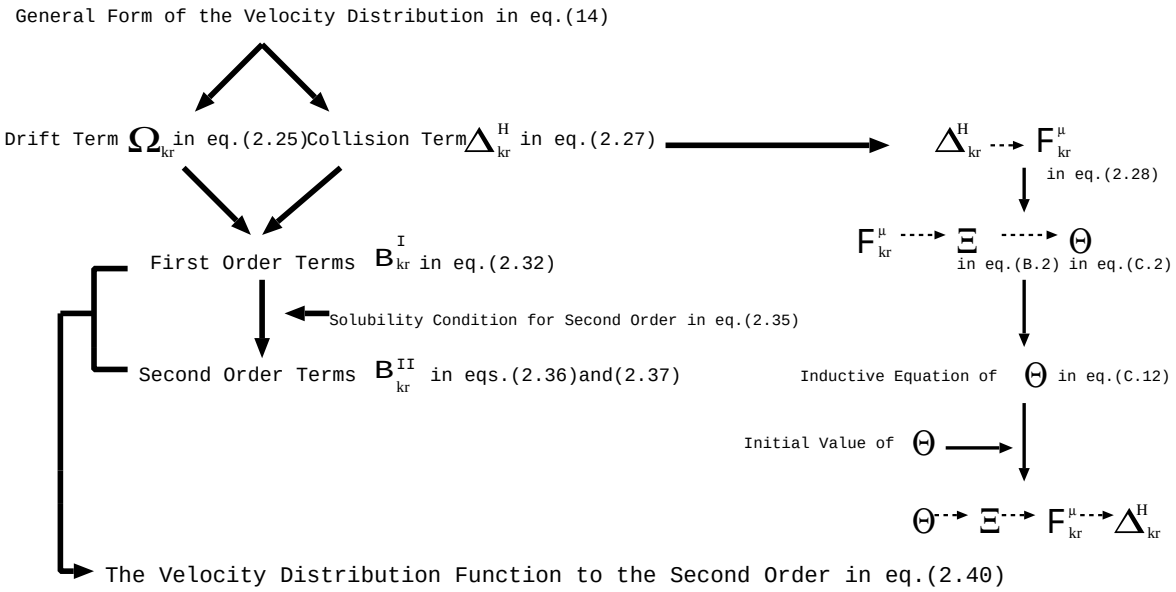

Figure 2.1: Algorithm of our calculation to derive the explicit form of the velocity distribution function of the steady-state Boltzmann equation for hard-core molecules to second order in a temperature gradient.

$Y_{kr}(\mathbf{c}_1)$ is a linear combination of spherical harmonic functions:

$$Y_{kr}(\mathbf{c}_1) = B_{kr}Y_k(\mathbf{c}_1) + 2\sum_{p=1}^{k}\frac{(k-p)!}{(k+p)!}[B_{kr}^{(p)}Y_k^{(p)}(\mathbf{c}_1) + C_{kr}^{(p)}Z_k^{(p)}(\mathbf{c}_1)], \quad (2.15)$$

where B_{kr}, $B_{kr}^{(p)}$ and $C_{kr}^{(p)}$ are coefficients to be determined. Introducing the normal spherical coordinate representation for $\mathbf{c}_1$, i.e. $c_{1x} = c_1\sin\theta\cos\phi$, $c_{1y} = c_1\sin\theta\sin\phi$ and $c_{1z} = c_1\cos\theta$, the spherical harmonic functions $Y_k(\mathbf{c}_1)$, $Y_k^{(p)}(\mathbf{c}_1)$ and $Z_k^{(p)}(\mathbf{c}_1)$ are expressed as

$$Y_k(\mathbf{c}_1) = \left(\frac{2\kappa T}{m}\right)^{\frac{k}{2}} c_1^k P_k(\cos\theta), \quad (2.16)$$

and

$$Y_k^{(p)}(\mathbf{c}_1) = (-1)^p\left(\frac{2\kappa T}{m}\right)^{\frac{k}{2}} c_1^k P_k^{(p)}(\cos\theta)\cos p\phi, \quad (2.17)$$

and

$$Z_k^{(p)}(\mathbf{c}_1) = (-1)^p\left(\frac{2\kappa T}{m}\right)^{\frac{k}{2}} c_1^k P_k^{(p)}(\cos\theta)\sin p\phi, \quad (2.18)$$

with the Legendre polynomial $P_k(\cos\theta)$ and the associated Legendre polynomial $P_k^{(p)}(\cos\theta)$.

Assumption of the velocity distribution function of eq.(2.13) has some mathematical advantages in our calculation. Firstly, it is sufficient to determine the coefficients B_{kr}, because $B_{kr}^{(p)}$ and $C_{kr}^{(p)}$ can be always determined from B_{kr} by a transformation of axes owing to the properties of the spherical harmonic functions (2.16), (2.17) and (2.18). We call B_{kr}, $B_{kr}^{(p)}$ and $C_{kr}^{(p)}$ the family of B_{kr}. Secondly, some important physical quantities are related to coefficients $B_{kr}, B_{kr}^{(p)}, C_{kr}^{(p)}$: *e.g.* the density (2.10), the temperature (2.11) and the zero mean flow (2.12) with f_1 in eq.(2.13) lead to the five equivalent conditions[25, 26]:

$$B_{00} = 1, \quad B_{10} = B_{10}^{(1)} = C_{10}^{(1)} = 0, \quad B_{01} = 0. \quad (2.19)$$

Similarly, the pressure tensor P_{ij} defined by

$$P_{ij} = \left(\frac{2\kappa T}{m}\right)^{\frac{5}{2}}\int_{-\infty}^{\infty}\mathrm{d}\mathbf{c}_1 m c_{1i}c_{1j}f_1, \quad (2.20)$$

for $i, j = x, y$ and z is related to the family of B_{20}, which is the only family in which Burnett was interested.[25]

The coefficients B_{kr} except for those in eq.(2.19) can be calculated as follows. Multiplying the steady-state Boltzmann equation (2.1) by

$$Q_{kr}(\mathbf{c}_1) \equiv (k + \frac{1}{2})\sqrt{\pi}(\frac{m}{2\kappa T})^{\frac{k}{2}} Y_k(\mathbf{c}_1) S^r_{k+\frac{1}{2}}(\mathbf{c}_1^2), \tag{2.21}$$

and then integrating over $(2\kappa T/m)^{1/2}\mathbf{c}_1$, it is found that

$$-\left(\frac{2\kappa T}{m}\right)^{\frac{1}{2}} < \mathbf{c}_1 \cdot \nabla Q_{kr} >_{av} + \nabla \cdot \left[\left(\frac{2\kappa T}{m}\right)^{\frac{1}{2}} < \mathbf{c}_1 Q_{kr} >_{av}\right] = \left(\frac{2\kappa T}{m}\right)^3 \int\int\int\int (Q'_{kr} - Q_{kr}) f_1 f_2 g b \mathrm{d}b \mathrm{d}\epsilon \mathrm{d}\mathbf{c}_2 \mathrm{d}\mathbf{c}_1, \tag{2.22}$$

where $< X >_{av}$ represents $(2\kappa T/m)^{3/2} \int X f_1 \mathrm{d}\mathbf{c}_1$, and Q'_{kr} represents the postcollisional Q_{kr}. We should calculate both sides of eq.(2.22) for every k and r, because eq.(2.22) leads to equations to determine B_{kr}, as will be shown in Appendices D and E.

For convenience, we introduce Ω_{kr} and Δ_{kr} as the left-hand and right-hand sides of eq.(2.22), respectively, i.e.

$$\Omega_{kr} \equiv -\left(\frac{2\kappa T}{m}\right)^{\frac{1}{2}} < \mathbf{c}_1 \cdot \nabla Q_{kr} >_{av} + \nabla \cdot \left[\left(\frac{2\kappa T}{m}\right)^{\frac{1}{2}} < \mathbf{c}_1 Q_{kr} >_{av}\right], \tag{2.23}$$

and

$$\Delta_{kr} \equiv \left(\frac{2\kappa T}{m}\right)^3 \int\int\int\int (Q'_{kr} - Q_{kr}) f_1 f_2 g b \mathrm{d}b \mathrm{d}b \mathrm{d}\epsilon \mathrm{d}\mathbf{c}_2 \mathrm{d}\mathbf{c}_1. \tag{2.24}$$

We will calculate Ω_{kr} and Δ_{kr} separately. The result of Ω_{kr} becomes

$$\begin{aligned} \Omega_{kr} &= \frac{n}{T}(\frac{2\kappa T}{m})^{\frac{1}{2}}[(r + \frac{k}{2})(D_{k,r}\partial_x T + E_{k,r}\partial_y T + G_{k,r}\partial_z T) \\ &- (D_{k,r-1}\partial_x T + E_{k,r-1}\partial_y T + G_{k,r-1}\partial_z T)] \\ &+ \partial_x\left[n(\frac{2\kappa T}{m})^{\frac{1}{2}} D_{k,r}\right] + \partial_y\left[n(\frac{2\kappa T}{m})^{\frac{1}{2}} E_{k,r}\right] + \partial_z\left[n(\frac{2\kappa T}{m})^{\frac{1}{2}} G_{k,r}\right], \end{aligned} \tag{2.25}$$

where $\partial_\mathrm{i} X$ denotes $\partial X/\partial \mathrm{i}$ for $\mathrm{i} = \mathrm{x}, \mathrm{y}$ and z. $D_{k,r}$, $E_{k,r}$ and $G_{k,r}$ are functions of the family of B_{kr}, as is written in Appendix A.

2.2.2 The collision term Δ_{kr}

Next, we calculate the collision term Δ_{kr} in eq.(2.24). We should specify the kind of interactions of molecules so as to perform the calculation of the collision term Δ_{kr}; the impact parameter b is explicitly determined by specifying the type of interaction. For hard-core molecules, the impact parameter b is given by the relation

$$b = d\cos\frac{\chi}{2}, \tag{2.26}$$

where d is the hard-core molecular diameter and χ is the scattering angle. (see Fig.1.1) Therefore, Δ_{kr} for hard-core molecules, i.e. Δ_{kr}^{H}, becomes[25]

$$\Delta_{kr}^{\mathrm{H}} = \frac{d^2}{2}\int_0^{\pi}[F_{kr}^1(\chi) - F_{kr}^1(0)]\sin\frac{\chi}{2}\cos\frac{\chi}{2}\mathrm{d}\chi, \tag{2.27}$$

where $F_{kr}^{\mu}(\chi)$ is defined as

$$F_{kr}^{\mu}(\chi) \equiv \left(\frac{2\kappa T}{m}\right)^3\int\int\int Q'_{kr}f_1f_2g^{\mu}\mathrm{d}\epsilon\mathrm{d}\mathbf{c}_2\mathrm{d}\mathbf{c}_1, \tag{2.28}$$

and we have used $F_{kr}^{\mu}(0) = (2\kappa T/m)^3\int\int\int Q_{kr}f_1f_2g^{\mu}\mathrm{d}\epsilon\mathrm{d}\mathbf{c}_2\mathrm{d}\mathbf{c}_1$. Note that $\chi = 0$ if $b > d$. For Maxwell molecules, the impact parameter b is given by the relation

$$b\mathrm{d}b = \frac{1}{g}H(\chi)\mathrm{d}\chi, \tag{2.29}$$

where $H(\chi)$ is a function of χ.[6, 22, 23, 24] Therefore, Δ_{kr} for Maxwell molecules, i.e. Δ_{kr}^{M}, becomes

$$\Delta_{kr}^{\mathrm{M}} = \int_0^{\pi}[F_{kr}^0(\chi) - F_{kr}^0(0)]H(\chi)\mathrm{d}\chi. \tag{2.30}$$

Since Δ_{kr}^{M} has been calculated by Schamberg[26], we will calculate only Δ_{kr}^{H} in this thesis. Schamberg's result for Δ_{kr}^{M} is briefly summarized in our web page.[140]

From eq.(2.27), it is sufficient to calculate $F_{kr}^1(\chi)$ for Δ_{kr}^{H}. The details of $F_{kr}^1(\chi)$ are written in Appendix B. Several explicit forms of Δ_{kr}^{H} are also demonstrated in Appendices D and E. From the definitions (2.23) and (2.24),

both sides of eq.(2.22) for arbitrary k and r can be calculated for hard-core molecules via

$$\Omega_{kr}^{\mathrm{H}} = \Delta_{kr}^{\mathrm{H}}, \tag{2.31}$$

which produces a set of simultaneous equations determining the coefficients B_{kr}, as is explained in Appendices D and E. Here Ω_{kr}^{H} denotes Ω_{kr} in eq.(2.25) for hard-core molecules.

2.2.3 Determination of B_{kr}

We will determine the first-order coefficients B_{kr}^{I} and the second-order coefficients B_{kr}^{II} in accordance with the previous two subsections, which corresponds to solving the integral equations (2.4) and (2.5), respectively. Here the upper suffices I and II are introduced to specify the order of B_{kr}. We have provided an example of our Mathematica program for calculating these coefficients.[140]

The First Order

We show the results of the first-order coefficients B_{kr}^{I} of which the solution of the integral equation (2.4), $\phi_1^{(1)}$, is composed. They can be written in the form:

$$B_{kr}^{\mathrm{I}} = \delta_{k,1} b_{1r} \frac{15}{16} \frac{\partial_z T}{\sqrt{2\pi} d^2 n T}. \tag{2.32}$$

Values of the constants b_{1r} are given in Table 2.1. The calculation of B_{kr}^{I} is explained in Appendix D. It is seen that B_{kr}^{I} is of the order of the Knudsen number K, which means that the mean free path of molecules should be much less than the characteristic length for changes in the macroscopic variables. Though Burnett derived B_{kr}^{I} only to 4th approximation, i.e. B_{kr}^{I} for $r \leq 4$, we have obtained B_{kr}^{I} for $r \leq 7$ in this thesis. This ensures the convergence of all the physical quantities which will be calculated in this thesis. It should be mentioned that our values of B_{kr}^{I} for $r \leq 4$ agree with Burnett's values[25]. Once B_{kr}^{I} have been calculated, $B_{kr}^{(1)\mathrm{I}}$ can be written down directly by replacing $\partial_z T$ by $\partial_x T$ by symmetry, owing to the properties of the spherical harmonic function[25]; $C_{kr}^{(1)\mathrm{I}}$ can also be obtained similarly

by replacing $\partial_z T$ by $\partial_y T$. Note that other terms, such as $B_{kr}^{(2)\mathrm{I}}$, do not appear because p in $B_{kr}^{(p)\mathrm{I}}$ must be k or less from eq.(2.15). Substituting all the first-order coefficients derived here into eq.(2.15), we can finally obtain the first-order velocity distribution function $f_1^{(1)}$.

Table 2.1: Numerical constants b_{1r} in eq.(2.32)

r	$r \leq 4$	$r \leq 5$	$r \leq 6$	$r \leq 7$
1	1.025	1.025	1.025	1.025
2	4.881×10^{-2}	4.889×10^{-2}	4.891×10^{-2}	4.892×10^{-2}
3	3.639×10^{-3}	3.698×10^{-3}	3.711×10^{-3}	3.715×10^{-3}
4	2.526×10^{-4}	2.838×10^{-4}	2.905×10^{-4}	2.922×10^{-4}
5	–	1.855×10^{-5}	2.123×10^{-5}	2.187×10^{-5}
6	–	–	1.284×10^{-6}	1.492×10^{-6}
7	–	–	–	8.322×10^{-8}

Solubility Conditions for $\phi_1^{(2)}$

Since the first-order velocity distribution function $f_1^{(1)}$ has been obtained, the solubility conditions of the integral equation (2.5) should be considered before we attempt to derive an expression for $\phi_1^{(2)}$. The solubility conditions for $\phi_1^{(2)}$, that is, eqs.(2.9) lead to the condition

$$\nabla \cdot \mathbf{J}^{(1)} = 0, \tag{2.33}$$

where $\mathbf{J}^{(1)}$, i.e. the heat flux for $f_1^{(1)}$, can be obtained as

$$\begin{aligned} \mathbf{J}^{(1)} &\equiv \left(\frac{2\kappa T}{m}\right)^3 \int_{-\infty}^{\infty} \mathrm{d}\mathbf{c}_1 \frac{m\mathbf{c}_1^2}{2} \mathbf{c}_1 f_1^{(1)} \\ &= -b_{11} \frac{75}{64} \left(\frac{\kappa T}{\pi m}\right)^{\frac{1}{2}} \frac{\kappa}{d^2} \nabla T, \end{aligned} \tag{2.34}$$

with the appropriate value for b_{11} listed in Table 2.1. It must be emphasized that, since $\mathbf{J}^{(2)}$, i.e. the heat flux for $f_1^{(2)}$, does not appear, the solubility conditions of the steady-state Boltzmann equation for $\phi_1^{(2)}$ lead to the heat

flux being constant to second order. From eqs.(2.33) and (2.34), we also obtain an important relation between $(\nabla T)^2$ and $\nabla^2 T$, namely

$$\frac{(\nabla T)^2}{2T} + \nabla^2 T = 0. \tag{2.35}$$

Owing to the relation (2.35), terms of $\nabla^2 T$ can be replaced by terms of $(\nabla T)^2$.

The Second Order

We write down the results of the second-order coefficients $B_{kr}^{\rm II}$ of which $\phi_1^{(2)}$ is composed. Using the relation (2.35), we can determine the second-order coefficients $B_{0r}^{\rm II}$ appearing in eq.(2.13) as

$$B_{0r}^{\rm II} = \frac{b_{0r}}{\pi d^4 n^2 T^2} (\nabla T)^2 . \tag{2.36}$$

Values for the constants b_{0r} are summarized in Table 2.2. The calculation of $B_{0r}^{\rm II}$ is shown in Appendix E. It must be emphasized that Burnett did not obtain the second-order coefficients $B_{0r}^{\rm II}$ because he was interested in only the coefficient $B_{20}^{\rm II}$ which is related to the pressure tensor P_{ij}.[25] The necessity of the second-order coefficients $B_{0r}^{\rm II}$ for the calculation of some physical quantities will be discussed later. We have calculated $B_{0r}^{\rm II}$ to 7th approximation, i.e. $B_{0r}^{\rm II}$ for $r \leq 6$ in this thesis.

Table 2.2: Numerical constants b_{0r} in eq.(2.36)

r	$r \leq 4$	$r \leq 5$	$r \leq 6$	$r \leq 7$	Maxwell's b_{0r}
2	4.434×10^{-1}	4.390×10^{-1}	4.381×10^{-1}	4.380×10^{-1}	$\frac{825}{1024}$
3	-4.935×10^{-2}	-5.342×10^{-2}	-5.413×10^{-2}	-5.429×10^{-2}	$-\frac{25}{256}$
4	–	-3.581×10^{-3}	-4.007×10^{-3}	-4.098×10^{-3}	0
5	–	–	-2.779×10^{-4}	-3.184×10^{-4}	0
6	–	–	–	-2.087×10^{-5}	0

The other second-order coefficients $B_{kr}^{\rm II}$ in eq.(2.15) can be written in the final form:

$$B_{kr}^{\rm II} = \frac{\delta_{k,2}}{\pi d^4 n^2 T^2} \left\{ b_{2r}^A \left[2\left(\partial_z T\right)^2 - \left(\partial_x T\right)^2 - \left(\partial_y T\right)^2 \right] + b_{2r}^B T \left[2\partial_z^2 T - \partial_x^2 T - \partial_y^2 T \right] \right\}. \tag{2.37}$$

Values for the constants b_{2r}^A and b_{2r}^B are summarized in Table 2.3. The calculation of $B_{kr}^{\rm II}$ is explained in Appendix E. Although Burnett obtained $B_{kr}^{\rm II}$ only to 4th approximation, i.e. $B_{kr}^{\rm II}$ for $r \leq 3$, we have obtained $B_{kr}^{\rm II}$ to 7th approximation, i.e. $B_{kr}^{\rm II}$ for $r \leq 6$ in the present thesis. Owing to the properties of the spherical harmonic function[25], $B_{kr}^{(1){\rm II}}$ can be obtained by replacing $2(\partial_z T)^2 - (\partial_x T)^2 - (\partial_y T)^2$ and $2\partial_z^2 T - \partial_x^2 T - \partial_y^2 T$ in eq.(2.37) by $6\partial_z T \partial_x T$ and $6\partial_z \partial_x T$, respectively, using an axis change. Similarly, $C_{kr}^{(1){\rm II}}$ can be obtained by replacing $2(\partial_z T)^2 - (\partial_x T)^2 - (\partial_y T)^2$ and $2\partial_z^2 T - \partial_x^2 T - \partial_y^2 T$ by $6\partial_z T \partial_y T$ and $6\partial_z \partial_y T$, respectively. $B_{kr}^{(2){\rm II}}$ can be obtained by replacing $2(\partial_z T)^2 - (\partial_x T)^2 - (\partial_y T)^2$ and $2\partial_z^2 T - \partial_x^2 T - \partial_y^2 T$ by $6[(\partial_x T)^2 - (\partial_y T)^2]$ and $6(\partial_x^2 T - \partial_y^2 T)$, respectively, via an axis change; $C_{kr}^{(2){\rm II}}$ by replacement by $12\partial_x T \partial_y T$ and $12\partial_x \partial_y T$, respectively. Note that other terms, *e.g.* $B_{kr}^{(3){\rm II}}$, do not appear because p in $B_{kr}^{(p){\rm II}}$ must be k or less, from eq.(2.15).

One can see that both of $B_{0r}^{\rm II}$ and $B_{kr}^{\rm II}$ are of the order of K^2. As is mentioned in Appendix E, we have found the fact that $B_{kr}^{\rm II}$ for $k = 4$, 6 and 8 do not appear, which strongly suggests that $B_{kr}^{\rm II}$ for all k greater than 2 do not appear. Thus, we expect $B_{kr}^{\rm II} = 0$ for $k \neq 2$ although Burnett[25] had believed that they would appear. We have calculated the second-order coefficients now, so that we finally obtain $f_1^{(2)}$ by substituting the second-order coefficients obtained here into eqs.(2.13) and (2.15).

Finally, we note that, though we have derived all the constants b_{1r}, b_{0r}^A, b_{0r}^B, b_{2r}^A and b_{2r}^B in forms of fractions, we have written them in forms of four significant figures in this thesis, since the forms of the fractions are too complicated.

The Velocity Distribution Functions to Second Order

The velocity distribution function for hard-core molecules which we have derived in this subsection valid to second order is now applied to a nonequilibrium steady-state system under the temperature gradient along x-axis. In

Table 2.3: Numerical constants b_{2r}^{A}(upper) and b_{2r}^{B}(lower) in eq.(2.37)

r	$r \leq 4$	$r \leq 5$	$r \leq 6$	$r \leq 7$
0	7.065×10^{-3}	7.312×10^{-3}	7.366×10^{-3}	7.380×10^{-3}
1	-1.654×10^{-1}	-1.647×10^{-1}	-1.646×10^{-1}	-1.646×10^{-1}
2	5.970×10^{-2}	6.040×10^{-2}	6.055×10^{-2}	6.059×10^{-2}
3	4.593×10^{-3}	5.071×10^{-3}	5.166×10^{-3}	5.190×10^{-3}
4	–	3.364×10^{-4}	3.824×10^{-4}	3.930×10^{-4}
5	–	–	2.495×10^{-5}	2.888×10^{-5}
6	–	–	–	1.726×10^{-6}

r	$r \leq 4$	$r \leq 5$	$r \leq 6$	$r \leq 7$
0	8.119×10^{-2}	8.117×10^{-2}	8.116×10^{-2}	8.116×10^{-2}
1	-7.380×10^{-2}	-7.388×10^{-2}	-7.390×10^{-2}	-7.390×10^{-2}
2	-7.001×10^{-3}	-7.090×10^{-3}	-7.108×10^{-3}	-7.113×10^{-3}
3	5.828×10^{-4}	6.469×10^{-4}	-6.595×10^{-4}	-6.626×10^{-4}
4	–	-4.897×10^{-5}	-5.541×10^{-5}	-5.687×10^{-5}
5	–	–	-3.796×10^{-6}	-4.365×10^{-6}
6	–	–	–	-2.716×10^{-6}

this case, the forms of $B_{0r}^{\rm II}$ in eqs.(2.36) becomes

$$B_{0r}^{\rm II} = \frac{b_{0r}}{\pi d^4 n^2 T^2} \left(\partial_x T\right)^2 , \tag{2.38}$$

and, using the relation (2.35), $B_{kr}^{\rm II}$ in eq.(2.37) can be transformed into a more simple form:

$$B_{kr}^{\rm II} = -\frac{\delta_{k,2} b_{2r}}{\pi d^4 n^2 T^2} \left(\partial_x T\right)^2 , \tag{2.39}$$

where values for the constants b_{2r} are summarized in Table 2.4. Our 4th approximation $B_{20}^{\rm II}$ deviates from Burnett's 4th approximation $B_{20}^{\rm II}$ by a factor 1.003. This deviation is considered to be due to errors in Burnett's calculation of the second and the third terms on the right-hand side of eq.(E.16). The other second-order terms become $B_{kr}^{(1){\rm II}} = C_{kr}^{(1){\rm II}} = C_{kr}^{(2){\rm II}} = 0$ and $B_{kr}^{(2){\rm II}} = 6\delta_{k,2} b_{2r} \left(\partial_x T\right)^2 / \pi d^4 n^2 T^2$.

From eqs.(2.13) and (2.15), the velocity distribution function of the steady-state Boltzmann equation for hard-core molecules to second order in the temperature gradient along x-axis can be written as

$$\begin{aligned} f &= f^{(0)} \left\{ 1 - \frac{4 J_x}{5 b_{11} n \kappa T} \left(\frac{m}{2\kappa T}\right)^{\frac{1}{2}} \sum_{r\geq 1} r! b_{1r} c_x \Gamma(r+\frac{5}{2}) S_{\frac{3}{2}}^r(\mathbf{c}^2) \right. \\ &\quad + \frac{4096 m J_x^2}{5625 b_{11}^2 n^2 \kappa^3 T^3} \left[\sum_{r\geq 2} r! b_{0r} \Gamma(r+\frac{3}{2}) S_{\frac{1}{2}}^r(\mathbf{c}^2) \right. \\ &\quad \left. \left. + \sum_{r\geq 0} r! b_{2r} (2c_x^2 - c_y^2 - c_z^2) \Gamma(r+\frac{7}{2}) S_{\frac{5}{2}}^r(\mathbf{c}^2) \right] \right\} , \end{aligned} \tag{2.40}$$

where the specific values for b_{1r}, b_{0r} and b_{2r} are found in Tables 2.1, 2.2 and 2.4, respectively, and J_x corresponds to the x component of the heat flux in eq.(2.34). Note that we have changed $\mathbf{c}_1$ to $\mathbf{c}$. Figure 2.2 gives the $\phi^{(2)}$ in eq.(2.40) scaled by $m J_x^2 / n^2 \kappa^3 T^3$ with the 4th, 5th, 6th and 7th approximation b_{0r}s and b_{2r}s. It should be mentioned that, as Fig.2.2 shows, the scaled $\phi^{(2)}$ in eq.(2.40) has not yet converged to 4th approximation, but seems to converge to 7th approximation. Figure 2.3 provides the explicit form of the scaled $\phi^{(2)}$ for hard-core molecules with 7th approximation b_{0r} and b_{2r}. It is seen that the scaled $\phi^{(2)}$ for hard-core molecules is strained symmetrically.

Table 2.4: Numerical constants b_{2r} in eq.(2.39)

r	$r \leq 4$	$r \leq 5$	$r \leq 6$	$r \leq 7$	Maxwell's b_{2r}
0	-3.353×10^{-2}	-3.327×10^{-2}	-3.322×10^{-2}	-3.320×10^{-2}	0
1	-1.285×10^{-1}	-1.278×10^{-1}	-1.277×10^{-1}	-1.276×10^{-1}	$\frac{75}{896}$
2	6.320×10^{-1}	6.394×10^{-2}	6.410×10^{-2}	6.414×10^{-2}	$\frac{125}{1536}$
3	4.884×10^{-3}	5.395×10^{-3}	5.496×10^{-3}	5.521×10^{-3}	0
4	–	3.609×10^{-4}	4.101×10^{-4}	4.214×10^{-4}	0
5	–	–	2.685×10^{-5}	3.106×10^{-5}	0
6	–	–	–	1.861×10^{-6}	0

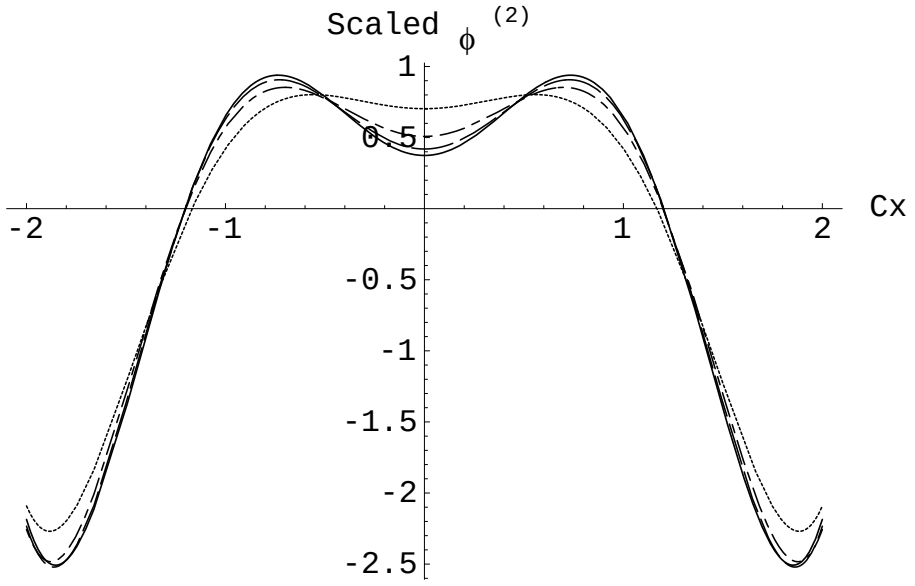

Figure 2.2: The scaled $\phi^{(2)}$s for hard-core molecules. The dotted line, the dash-dotted line, the long-dashed line and the solid line correspond to the scaled $\phi^{(2)}$s for hard-core molecules with the 4th, 5th, 6th and 7th approximation b_{0r}s and b_{2r}s, respectively. Note that we put $c_y = c_z = 0$.

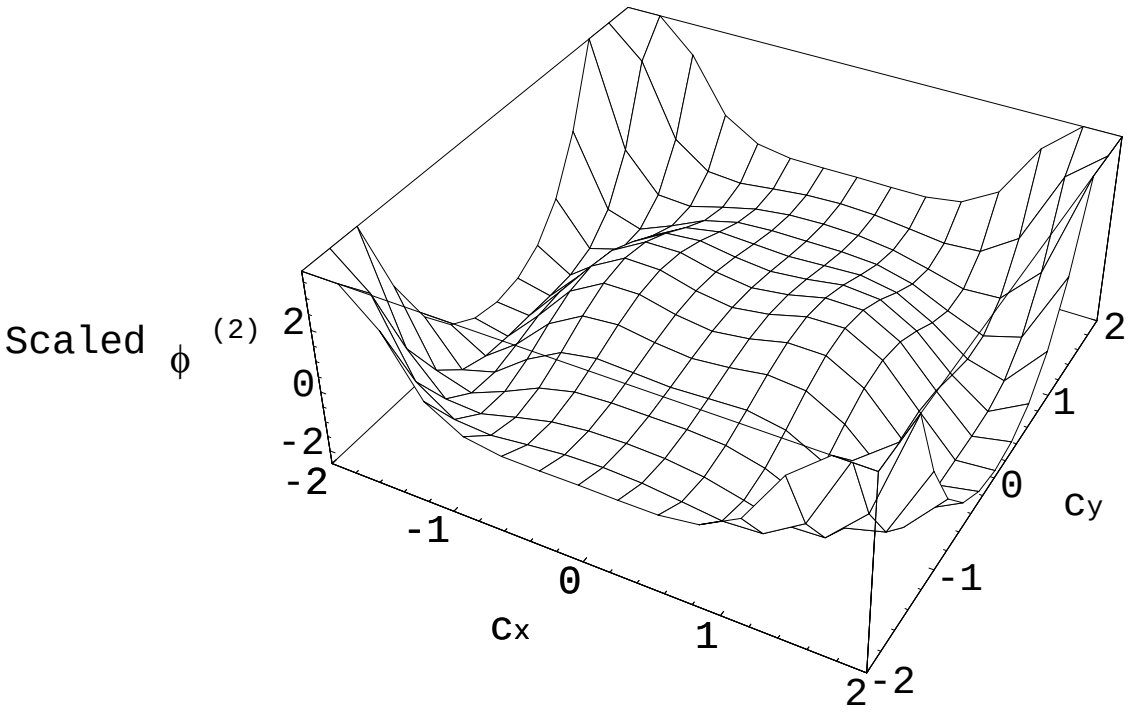

Figure 2.3: The scaled $\phi^{(2)}$ for hard-core molecules with 7th approximation b_{0r} and b_{2r}. Note that we put $c_z = 0$.

In order to compare the macroscopic quantities for hard-core molecules with those for Maxwell molecules, we also adopt the velocity distribution function for Maxwell molecules derived by Schamberg[26] for our calculation of the macroscopic quantities. We apply Schamberg's velocity distribution function to a nonequilibrium steady-state system under the temperature gradient along x-axis, that is, we take out the differential coefficients with respect to time t from Schamberg's velocity distribution function and also use the solubility condition (2.33) for Maxwell molecules. The precise velocity distribution function of the steady-state Boltzmann equation for Maxwell molecules to second order finally becomes[26]

$$\begin{aligned} f &= f^{(0)}\left\{1-\frac{4J_x}{5n\kappa T}(\frac{m}{2\kappa T})^{\frac{1}{2}}c_x\Gamma(\frac{7}{2})S^1_{\frac{3}{2}}(\mathbf{c}^2)\right. \\ &\quad +\frac{4096mJ_x^2}{5625n^2\kappa^3T^3}\left[\sum_{r=2,3} r!b_{0r}\Gamma(r+\frac{3}{2})S^r_{\frac{1}{2}}(\mathbf{c}^2)\right. \\ &\quad \left.\left.+\sum_{r=1,2} r!b_{2r}(2c_x^2-c_y^2-c_z^2)\Gamma(r+\frac{7}{2})S^r_{\frac{5}{2}}(\mathbf{c}^2)\right]\right\}, \end{aligned} \tag{2.41}$$

where the specific values for b_{0r} and b_{2r} are found in Tables 2.2 and 2.4, respectively. As can be seen from eqs.(2.40) and (2.41), the explicit form of the velocity distribution function for hard-core molecules becomes the sum of an infinite series of Sonine polynomials, while the precise form of the velocity distribution function for Maxwell molecules is the sum of five Sonine polynomials.

2.3 The Chapman-Enskog Solution of the Steady-State BGK Equation to second order

In this thesis, we also adopt the precise expression of the velocity distribution function for the steady-state BGK equation to second order. We introduce the velocity distribution function for the steady-state BGK equation to second order by the Chapman-Enskog method.[66, 67, 68, 69, 70]

The steady-state BGK equation is written as

$$v_x\partial_x f = \frac{f_{LE}-f}{\tau}, \tag{2.42}$$

where the relaxation time τ dependent on position x through the density $n(x)$ and the temperature $T(x)$. It should be mentioned that, for the conservation laws, the collision term for the steady-state BGK equation, the right-hand side of eq.(2.42), must satisfy

$$\int \Phi_{\rm i} f_{LE} d\mathbf{v} = \int \Phi_{\rm i} f d\mathbf{v}, \tag{2.43}$$

with the five collision invariants $\Phi_{\rm i}$ introduced in eq.2.8. Equation (2.43) with the definitions of the density (2.10), the temperature (2.11) and the zero mean flow (2.12) leads to the usual local equilibrium velocity distribution function $f_{LE} = f_{LE}(x, \mathbf{v}) = n(x)(m/2\pi\kappa T(x))^{3/2} \exp[-m\mathbf{v}^2/2\kappa T(x)]$. The velocity distribution function f can be expanded as:

$$f = f^{(0)} + f^{(1)} + f^{(2)} + \cdots, \tag{2.44}$$

with $f^{(0)} \equiv f_{LE}$. Substituting eq.(2.44) into the steady-state BGK equation (2.42), we arrive at the following set of equations:

$$-\frac{f^{(1)}}{\tau} = v_x \partial_x f^{(0)}, \tag{2.45}$$

to first order and

$$-\frac{f^{(2)}}{\tau} = v_x \partial_x f^{(1)}, \tag{2.46}$$

to second order. It is found that equation (2.45) with the requirement (2.43) leads to $n\kappa T$ being uniform, and that equation (2.46) with the requirement (2.43) leads to heat flux J_x calculated from eq.(4.5) being uniform. From eqs.(2.45) and (2.46), the velocity distribution function to second order for the steady-state BGK equation becomes

$$f = f^{(0)}\{1 - \frac{3J_x}{2n\kappa T}\left(\frac{\pi m}{2\kappa T}\right)^{\frac{1}{2}} c_x S^1_{\frac{3}{2}}(\mathbf{c}^2) + \frac{21\sqrt{\pi} m J_x^2}{5n^2\kappa^3 T^3} {c_x}^2 S^2_{\frac{3}{2}}(\mathbf{c}^2)\}, \tag{2.47}$$

with the *constant* heat flux $J_x = -5n\kappa^2 T\tau\partial_x T/2m$ and $S^p_k(X)$ the Sonine polynomials.

It has been proved that the Chapman-Enskog solution (2.47) is asymptotically correct to second order: the expression (2.47) is identical with the

velocity distribution function to second order reduced from the general form of the the Chapman-Enskog solution for the steady-state BGK equation to arbitrary order.[66, 67, 68, 69, 70] The first-order Chapman-Enskog solution for the steady-state BGK equation is identical to that for the steady-state Boltzmann equation for Maxwell molecules[59], while the second-order Chapman-Enskog solutions are different from each other. The result, eq.(2.47), also differs from the velocity distribution function for the BGK equation discussed by Trilling[74].

2.4 Direct comparison of the scaled $\phi^{(2)}$

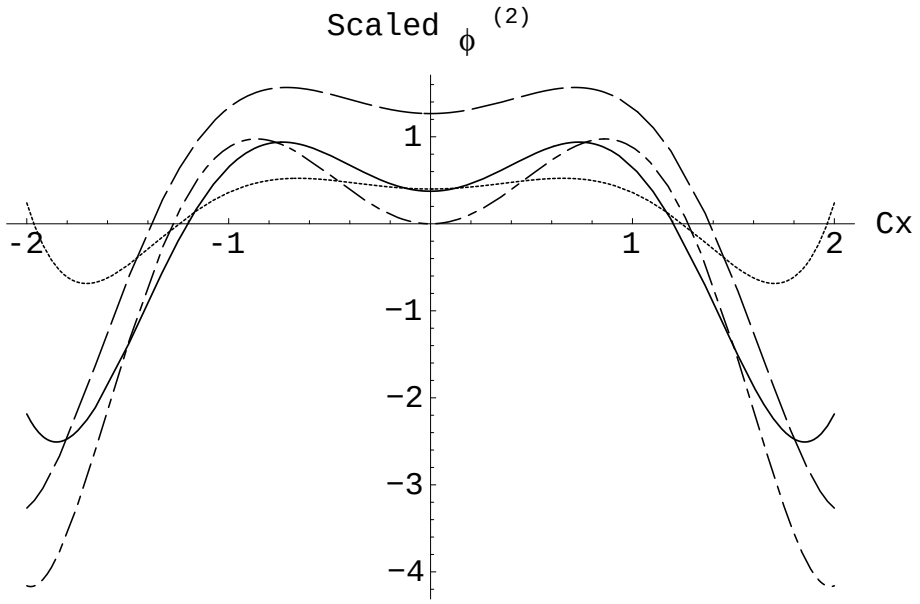

Figure 2.4: Direct comparison of the scaled $\phi^{(2)}$ for hard-core molecules with those for Maxwell molecules, the steady-state BGK equation and information theory. The solid line, the long-dashed line, the dash-dotted line and the dotted line correspond to the scaled $\phi^{(2)}$s for hard-core molecules, Maxwell molecules, the steady-state BGK equation and information theory, respectively. Note that we put $c_y = c_z = 0$.

Figure 2.4 exhibits the direct comparison of the scaled $\phi^{(2)}$s for hard-

core molecules (2.40) to 7th approximation with those for Maxwell molecules (2.41), the steady-state BGK equation (2.47) and information theory (4.9). Note that the derivation of $\phi^{(1)}$ and $\phi^{(2)}$ for information theory will be explained in Sec.4.1. We have found that, as Fig.2.4 explicitly shows, the second-order velocity distribution function for hard-core molecules (2.40) definitely differs from the others.

2.5 Nonlinear Nonequilibrium Transport Phenomena

We can introduce the general form of the heat flux as

$$J_x = -\varpi T^{\varphi} \partial_x T, \tag{2.48}$$

where φ indicates temperature dependence of the thermal conductivity and ϖ is a constant that depends upon microscopic models. J_x is constant from the solubility condition (2.33). For example, φ is calculated as 1/2 for hard-core molecules and 1 for Maxwell molecules; ϖ is determined as $75 b_{11} \kappa (\kappa/\pi m)^{1/2}/64 d^2$ with $b_{11} \simeq 1.025$ for hard-core molecules (see eq.(2.34)) and $5\kappa^2 (2m/G)^{1/2}/4A$ for Maxwell molecules[24, 28], where G is the constant of proportionality between the intermolecular force and the reciprocal fifth power of the distance, and A is a number constant erroneously evaluated as 1.3682 by Maxwell[22, 23] and recalculated as 1.3700 by Chapman[141]. Note that φ and ϖ cannot be determined explicitly from the BGK equation. From eq.(2.48), the temperature profile $T(x)$ in the nonequilibrium steady state can be determined as

$$\begin{aligned} T(x) &= [T(0)^{\varphi+1} - (\varphi+1)\frac{J_x}{\varpi} x]^{\frac{1}{\varphi+1}} \\ &\simeq T(0)[1 - \frac{J_x}{\varpi T(0)^{\varphi+1}} x - \frac{\varphi J_x^2}{2\varpi^2 T(0)^{2\varphi+2}} x^2], \end{aligned} \tag{2.49}$$

to second order. The temperature profile $T(x)$ becomes nonlinear except for $\varphi = 0$. This fact is in accord with a numerical result that a temperature profile becomes nonlinear as the heat flux becomes larger.[142]

Using eq.(2.20), the pressure tensor P_{ij} in the nonequilibrium steady state

can be obtained as

$$P_{ij} = n\kappa T[\delta_{ij} + \lambda_P^{ij}\frac{mJ_x^2}{n^2\kappa^3 T^3}], \tag{2.50}$$

with the unit tensor δ_{ij} and the tensor components λ_P^{ij} given in Table 2.5. Note that the off-diagonal components of λ_P^{ij} are zero and $\lambda_P^{yy} = \lambda_P^{zz}$ is satisfied. The values of λ_P^{ij} for 7th approximation b_{1r}, b_{0r} and b_{2r} for hard-core molecules, i.e. 7th approximation λ_P^{ij} seems to be converged to three significant figures, as can be seen from Table 2.5. We find that λ_P^{ij} for hard-core molecules differs from that for Maxwell molecules not only quantitatively but also qualitatively: $\lambda_P^{xx} \neq \lambda_P^{yy} = \lambda_P^{zz}$ for hard-core molecules in the nonequilibrium steady state, while $\lambda_P^{xx} = \lambda_P^{yy} = \lambda_P^{zz} = 0$ for Maxwell molecules. The latter results was also reported in ref.[28]. For hard-core molecules, P_{xx} becomes smaller than P_{yy} and P_{zz} regardless of the sign of J_x. It is also important that, since $n\kappa T$ is required to be uniform from the solubility conditions for $\phi^{(1)}$ in eq.(2.7), we find from eq.(2.49) that P_{ij} in eq.(2.50) is uniform to second order in the steady state. Additionally, since the temperature profile $T(x)$ has already been given in eq.(2.49), we can determine the density profile $n(x)$ to second order for uniform P_{ij}. Note that the equation of state in the nonequilibrium steady state is not modified to first order, and that λ_P^{ij} for the steady-state BGK equation is identical with that for Maxwell molecules.

Table 2.5: Numerical constants for the macroscopic quantities: the ith approximation quantities for hard-core molecules and the exact values for Maxwell molecules and the steady-state BGK equation.

ith	λ_P^{xx}	λ_P^{yy}	λ_S
4th	-4.647×10^{-2}	2.324×10^{-2}	-2.034×10^{-1}
5th	-4.610×10^{-2}	2.305×10^{-2}	-2.035×10^{-1}
6th	-4.602×10^{-2}	2.301×10^{-2}	-2.035×10^{-1}
7th	-4.600×10^{-2}	2.300×10^{-2}	-2.035×10^{-1}
Maxwell	0	0	$-\frac{1}{5}$
BGK equation	0	0	$-\frac{1}{5}$

Each component of the kinetic temperature in the nonequilibrium steady state, i.e. $T_{\rm i}$ for ${\rm i} = x, y$ and z is calculated as

$$\frac{n\kappa T_{\rm i}}{2} \equiv \left(\frac{2\kappa T}{m}\right)^{\frac{5}{2}} \int_{-\infty}^{\infty} {\rm d}\mathbf{c} \frac{m c_{\rm i}^2}{2} f, \tag{2.51}$$

which leads to

$$T_{\rm i} = T[1 + \lambda_P^{\rm ii} \frac{m J_x^2}{n^2 \kappa^3 T^3}], \tag{2.52}$$

for ${\rm i} = x, y$ and z. Values for the constants in the second-order term $\lambda_P^{\rm ii}$ are the same as $\lambda_P^{\rm ij}$ for ${\rm i} = {\rm j}$ given in Table 2.5. Since $n\kappa T$ and J_x are uniform, we see that the correction term of $T_{\rm i}$ in eq.(2.52) is independent of x. For hard-core molecules, T_x becomes smaller than T_y and T_z regardless of the sign of J_x, which means that the motion of hard-core molecules along the heat flux becomes dull. We note that $T_{\rm i}$ for the steady-state BGK equation is identical with that for Maxwell molecules, and that, to first order, $T_{\rm i}$ for hard-core molecules is isotropic.

The Shannon entropy in the nonequilibrium steady state S is defined via

$$\begin{aligned} S &\equiv -\kappa \left(\frac{2\kappa T}{m}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} {\rm d}\mathbf{c} f \log f \\ &= -n\kappa \log \left[n \left(\frac{m}{2\pi\kappa T}\right)^{\frac{3}{2}} \right] + \frac{3}{2} n\kappa + \lambda_S \frac{m J_x^2}{n\kappa^2 T^3}. \end{aligned} \tag{2.53}$$

Values for the constant λ_S are given in Table 2.5: λ_S for 7th approximation b_{1r}, b_{0r} and b_{2r} for hard-core molecules, i.e. 7th approximation λ_S seems to converge to four significant figures, see Table 2.5. It is found that λ_S for hard-core molecules is close to that for Maxwell molecules, while the latter is identical with that for the steady-state BGK equation. Note that the Shannon entropy in the nonequilibrium steady state is not modified to first order.

2.6 Discussion and Conclusion

Although the Chapman-Enskog method is widely accepted and used as a method to solve the Boltzmann equation, the following claims have been presented for its second-order solution.

(i) The linearized Burnett equation obtained by the Chapman-Enskog method does not satisfy Onsager's reciprocal theorem.[44]

(ii) It is difficult to give physical meanings to the first differential boundary conditions such as $\partial T/\partial x$ which arise from the second-order Chapman-Enskog solutions.[5, 15]

(iii) Solutions of the Burnett equation derived by the Chapman-Enskog method are unstable to disturbances of small wavelength whose length is less than the order of a mean free path.[143, 144, 145]

For (i), Romero and Velasco have reported that Onsager's reciprocal theorem extended by treating a heat flux as a thermodynamic variable can be satisfied with the linearized Burnett equation. [44] We have also confirmed that, in the case of the steady state, the linearized Burnett equation is consistent with usual Onsager's reciprocal theorem. Researchers who applaud the Hilbert method consider the claim (ii) is the most crucial problem for the Chapman-Enskog method.[5, 15] The Hilbert method does not face this problem because no higher-order differential solutions appear in the method. However, we have found that, by the relation (2.35) for the steady state, the second differential terms of $\nabla^2 T$ can be replaced by the first differential terms of $(\nabla T)^2$. Thus, it is not necessary to consider the differential boundary condition in the case for the steady state. For (iii), because the small parameter of the Chapman-Enskog expansion is the Knudsen number $K = l/L \ll 1$ with the mean free path l and the characteristic length L for changes in the macroscopic variables, the disturbances of small wavelength of the order of a mean free path are physically inconsistent and inappropriate treatments. We notice that numerical solutions of the Burnett equation should be performed with grids whose length is larger than the order of the mean free path.

Above all, Fushiki has recently demonstrated that our analytical second-order solution of the steady-state Boltzmann equation for hard-core molecules agrees well with results of his numerical experiment.[32] We introduce his graphical results in Fig.2.5. The blue line represents his MD result of $f - f^{(0)}$, while the red one exhibits our analytical result of $f^{(1)} + f^{(2)}$ in eq.(2.40). The details of his Molecular Dynamics(MD) simulation will be given in ref.[32]. We emphasize that the numerical result $f - f^{(0)}$ becomes asymmetric and definitely deviates from the analytical result of $f^{(1)}$ shown by the green line. It

can be concluded that the significant effect of the second-order solution of the steady-state Boltzmann equation is detected by the numerical experiment. It is also noteworthy that the good agreement between the analytical and numerical results is still observed even when the Knudsen number is up to about 0.2. The validity of the Chapman-Enskog method has been confirmed now, so that it is needed to derive the explicit second-order solution by the Grad method and compare it with our result by the Chapman-Enskog method, which will contribute to an important understanding of the relation between the two methods.

On the other hand, for extremely high density, the divergences of the second-order transport coefficients even in three dimension have been reported.[38, 39, 40] Using a lowest ring-collision summation, Ernst and Dorfman predicted the divergences by showing that the higher-order hydrodynamic frequencies have the nonanalytic dependence on wave number which corresponds to the Knudsen number.[38] This prediction was confirmed in the higher-order self-diffusion coefficient by Dufty and Mclennan who also used the lowest-density ring operator.[40] Although efficiency of the second-order coefficients has been experimentally demonstrated for moderately dense gases in shock wave and sound propagation phenomena[10, 53, 54, 55, 56, 57, 58], the above results imply the nonexistence of the nonlinear nonequilibrium thermodynamics which focuses on the second-order effects of the nonequilibrium fluxes. However, we suggest that transport phenomena in extremely high density gases may not be described only by the lowest-ring collision approximation, that is, other contributions to the the second-order transport coefficients must be considered for the estimation of them. The consideration possibly leads to the convergence of the second-order transport coefficients. The divergence may also be attributed to invalidity of a definition of the second-order diffusion coefficient adopted in ref.[40].

As was mentioned above, the validity of the steady-state Boltzmann equation has been confirmed even in the *local nonequilibrium state* by Fushiki.[32] It is important to consider what conditions make the Boltzmann equation hold, that is, what conditions make the assumption of molecular chaos valid. Of course one is the Boltzmann-Grad limit, $nd^3 \ll 1$. The other is also indicated implicitly by Reichl who assumed that, in order to derive the Boltzmann equation, the distribution functions do not change appreciably in *a small phase space*.[30] We suggest that her assumption corresponds to the condition $l \ll L$, and that this condition is also essential for the Boltzmann

equation. This suggestion means that the Boltzmann equation is valid even in the *local nonequilibrium state* so long as the condition $l \ll L$ holds. If $l \sim L$, thermodynamic quantities and the velocity distribution function of molecules definitely change during a mean free path, so that molecules must feel a kind of correlation through one collision process. We think that the correlation breaks the validity of the assumption of molecular chaos and makes the Boltzmann equation invalid. Our suggestion may be related to the divergence which appears in the Chapman-Enskog expansion to infinite order[66, 67, 68, 69, 70], and the instability of the Burnett equation to disturbances of the order of a mean free path.[143, 144, 145]

We have found that there are qualitative differences between hard-core molecules and Maxwell molecules in the nonequilibrium steady state: second-order corrections appear for hard-core molecules in the pressure tensor P_{ij} and the kinetic temperature $T_{\rm i}$, while no correction to these quantities appears for Maxwell molecules, as Table 2.5 shows. It should be noted that the qualitative differences between hard-core molecules and Maxwell molecules still appear no matter which boundary condition is adopted, that is, the isotropy and the anisotropy of the pressure tensor in eq.(2.50) and the kinetic temperature in eq.(2.52) are not affected by any kinds of boundary conditions. It is conjectured that these differences are attributed to the special nature of Maxwell molecules: Δ_{kr} for Maxwell molecules, i.e. $\Delta_{kr}^{\rm M}$ is independent of the magnitude of the relative velocity g, because $F_{kr}^0(\chi)$ is independent of g. In general, Δ_{kr} for molecules which interact with each other by a central force depends on g, because $F_{kr}^\mu(\chi)$ generally depends on g. Therefore, it may be suggested that molecules which interact via a central potential still have the qualitative differences from Maxwell molecules: second-order corrections in pressure tensor P_{ij} and kinetic temperature $T_{\rm i}$ may appear also for such molecules as well as hard-core molecules.

It is also found that the pressure tensor P_{ij} and the kinetic temperature $T_{\rm i}$ for the steady-state BGK equation are qualitatively different from those for the steady-state Boltzmann equation for hard-core molecules but agree with those for the steady-state Boltzmann equation for Maxwell molecules, as illustrated in Table 2.5. Since the Chapman-Enskog solution of the steady-state BGK equation is asymptotically correct[66, 67, 68, 69, 70], we may conclude that the steady-state BGK equation does not capture the essence of hard-core molecules, but captures that of Maxwell-type molecules. This conclusion indicates the possibility that even the exact solution of the steady-

state BGK equation can be applied only to Maxwell-type molecules. The qualitative agreements between the steady-state BGK equation and Maxwell molecules are due to the fact that the collision frequency of the former is independent of the relative speed g as well as the latter, which was indicated by Prof. Santos in a private discussion. In other words, we can state that g-dependency cannot be absorbed in the single relaxation time τ. Therefore, we propose that the steady-state BGK equation could capture the essence of other molecules than Maxwell molecules if one made the relaxation time depend on g or if one developed the steady-state BGK equation with multi-relaxation times. We also notice that other kinetic models such as the lattice Boltzmann method[146] which significantly simplify the collision term of the Boltzmann equation could not apply to fluid dynamics beyond the Navier-Stokes equation.

Finally, we consider the possibility of the existence of a universal velocity distribution function in the nonequilibrium steady state. When we express the velocity distribution function for hard-core molecules to second order using the heat flux J_x as in eq.(2.40), it becomes independent of the diameter d of the hard-core molecules. However, the explicit form of the velocity distribution function for hard-core molecules (2.40) definitely differs from the precise form of the velocity distribution function for Maxwell molecules (2.41) or that for the steady-state BGK equation (2.47) as Fig.2.4 shows. Actually, as was mentioned above, we have shown that the results calculated from the former are qualitatively different from those calculated from the others. These results indicate that the characteristics of microscopic models appear in the *local nonequilibrium state* and affect even qualitatively the macroscopic quantities. It can be concluded that a universal velocity distribution function does not exist in the *local nonequilibrium state* even if the velocity distribution function is expressed only in terms of the macroscopic quantities.[59]

Chapter 3

Contributions of Steady Heat Conduction to the Rate of Chemical Reaction

3.1 Calculation of the Rate of Chemical Reaction

In this chapter, we calculate the rate of chemical reaction (1.7) with the line-of-centers model (1.8) using the explicit velocity distribution function of the steady-state Boltzmann equation for hard-core molecules to second order (2.40).[59, 130] Substituting the expanded form of the velocity distribution function to second order as in eq.(2.2) into eq.(1.7), we obtain

$$R = R^{(0)} + R^{(1)} + R^{(2)}, \tag{3.1}$$

up to second order. The zeroth-order term of R,

$$R^{(0)} = \int d\mathbf{v} \int d\mathbf{v}_1 \int d\mathbf{\Omega} \int f^{(0)} f_1^{(0)} g\sigma(g) = 4n^2\sigma^2 \left(\frac{\pi\kappa T}{m}\right)^{\frac{1}{2}} e^{-\frac{E^*}{\kappa T}}, \tag{3.2}$$

corresponds to the rate of chemical reaction of the equilibrium theory. Similarly, the first-order term of R is obtained as

$$R^{(1)} = \int d\mathbf{v} \int d\mathbf{v}_1 \int d\mathbf{\Omega} \int f^{(0)} f_1^{(0)} [\phi^{(1)} + \phi_1^{(1)}] g\sigma(g), \tag{3.3}$$

where $R^{(1)}$ does not appear because $\phi^{(1)}$ is an odd functions of $\mathbf{c}$, as will be shown in the next section. The second-order term of R, *i.e.* $R^{(2)}$, is divided into

$$R^{(2,A)} = \int d\mathbf{v} \int d\mathbf{v}_1 \int d\mathbf{\Omega} \int f^{(0)} f_1^{(0)} \phi^{(1)} \phi_1^{(1)} g\sigma(g), \tag{3.4}$$

and

$$R^{(2,B)} = \int d\mathbf{v} \int d\mathbf{v}_1 \int d\mathbf{\Omega} \int f^{(0)} f_1^{(0)} [\phi^{(2)} + \phi_1^{(2)}] g\sigma(g). \tag{3.5}$$

Since the integrations (3.4) and (3.5) have the cutoff from eq.(1.8), the explicit forms of $\phi^{(1)}$ and $\phi^{(2)}$ of the steady-state Boltzmann equation for hard-sphere molecules are required to calculate $R^{(2,A)}$ and $R^{(2,B)}$, respectively.

In Fig. 2.2, we have confirmed that $\phi^{(2)}$ does not converge to 4th Sonine approximation but both of $\phi^{(1)}$ and $\phi^{(2)}$ almost converge to 7th Sonine approximation[130], so that, in this thesis, we will show the results calculated from $\phi^{(1)}$ and $\phi^{(2)}$ for 7th approximation of Sonine polynomials. We note that Burnett had determined only b_{1r} and b_{2r} to 4th Sonine approximation: b_{2r} is related to the second-order pressure tensor.[25] Therefore, we could not calculate the effect of steady heat flux on the rate of chemical reaction with the line-of-centers model if we did not derive the explicit forms of $\phi^{(1)}$ and $\phi^{(2)}$, especially b_{0r} in the previous chapter. In order to compare the results from the steady-state Boltzmann equation with those from the steady-state BGK equation and information theory, we also use the explicit forms of $\phi^{(1)}$ and $\phi^{(2)}$. The expressions of $\phi^{(1)}$ and $\phi^{(2)}$ for the steady-state BGK equation are written in eq.(2.47), while those for information theory will be shown in eq.(4.9) in the next chapter.

3.2 Local Nonequilibrium Effects on the Rate of Chemical Reaction

Inserting $\phi^{(1)}$ and $\phi^{(2)}$ of eq.(2.40) for the steady-state Boltzmann equation for hard-core molecules, eq.(2.47) for the steady-state BGK equation and eq.(4.9) for information theory into eqs.(3.4) and (3.5), and performing the integrations with the chemical reaction cross-section (1.8), we finally obtain the nonequilibrium effects on the rate of chemical reaction based on the line-

of-centers model. The expressions of $R^{(2,A)}$ and $R^{(2,B)}$ become

$$R^{(2,A)} = \frac{\sigma^2 m J_x^2}{\kappa^3 T^3} \left(\frac{\pi\kappa T}{m}\right)^{\frac{1}{2}} e^{-\frac{E^*}{\kappa T}} \{\sum_{r\geq 0} \alpha_r \left(\frac{E^*}{\kappa T}\right)^r\}, \tag{3.6}$$

and

$$R^{(2,B)} = \frac{\sigma^2 m J_x^2}{\kappa^3 T^3} \left(\frac{\pi\kappa T}{m}\right)^{\frac{1}{2}} e^{-\frac{E^*}{\kappa T}} \{\sum_{r\geq 0} \beta_r \left(\frac{E^*}{\kappa T}\right)^r\}, \tag{3.7}$$

respectively. The numerical values for α_r and β_r are listed in Tables 3.1 and 3.2, respectively. We have found that $R^{(2,B)}$ for the steady-state Boltzmann equation is determined only by the terms of b_{0r} in $\phi^{(2)}$ of eq.(2.40) which Burnett[25] had not derived: the terms of b_{0r} we have derived in ref.[130] are indispensable for the calculation of $R^{(2,B)}$.

Table 3.1: Numerical constants α_r in eq.(3.6).

r	Boltzmann Eq.	BGK Eq. and Information Theory
0	-2.292×10^{-2}	$-\frac{1}{50}$
1	-1.448×10^{-1}	$-\frac{3}{25}$
2	3.223×10^{-1}	$\frac{6}{25}$
3	-9.834×10^{-2}	$-\frac{4}{75}$
4	7.919×10^{-3}	–
5	-6.752×10^{-4}	–
6	5.298×10^{-5}	–
7	-3.584×10^{-6}	–
8	2.039×10^{-7}	–
9	-9.599×10^{-9}	–
10	3.613×10^{-10}	–
11	-1.032×10^{-11}	–
12	2.110×10^{-13}	–
13	-2.887×10^{-15}	–
14	2.352×10^{-17}	–
15	-8.578×10^{-20}	–

Table 3.2: Numerical constants β_r in eq.(3.7).

r	Boltzmann Eq.	BGK Eq.	Information Theory
0	-1.361×10^{-1}	$-\frac{11}{75}$	$-\frac{19}{150}$
1	-5.094×10^{-1}	$-\frac{38}{75}$	$-\frac{7}{15}$
2	3.968×10^{-1}	$\frac{4}{15}$	$\frac{26}{75}$
3	5.805×10^{-2}	$\frac{8}{75}$	$\frac{4}{75}$
4	-2.811×10^{-3}	–	–
5	1.039×10^{-4}	–	–
6	-1.808×10^{-6}	–	–

The explicit expressions in eqs.(3.6) and (3.7) for information theory were already given by Fort and Cukrowski.[60, 100] Though they were interested in forms of $Q_A \equiv R^{(2,A)}/R^{(0)}$ and $Q_B \equiv R^{(2,B)}/R^{(0)}$[60, 100], in the present thesis, we focus on the nonequilibrium effects on the rate of chemical reaction in the forms of $R^{(2,A)}$ and $R^{(2,B)}$. This is because the forms of Q_A and Q_B for the steady-state Boltzmann equation do not converge even when we adopt any higher order approximation of Sonine polynomials. The upper limit of r in eqs.(3.6) and (3.7) is directly related to the order of the approximation of Sonine polynomials in eq.(2.40): $S_k^r(\mathbf{c}^2)$ includes the term of $\mathbf{c}^{2r}$. We emphasize that, however, the values of $R^{(2,A)}$ and $R^{(2,B)}$ for the steady-state Boltzmann equation converge to 7th approximation of Sonine polynomials. It should be also mentioned that there appear artificial qualitative differences in both Q_A and Q_B for the steady-state Boltzmann equation, the steady-state BGK equation and information theory for large $E^*/\kappa T$.

The graphical results of $R^{(2)}$ compared with those of $R^{(2,A)}$ are provided in Fig.3.1. Both of $R^{(2)}$ and $R^{(2,A)}$ in Fig.3.1 are scaled by $\pi^{1/2}d^2m^{1/2}J_x^2/\kappa^{5/2}T^{5/2}$. Note that $R^{(2)}$ is the sum of $R^{(2,A)}$ and $R^{(2,B)}$ in eqs.(3.6) and (3.7). As Fig.3.1 shows, it is clear that $R^{(2,B)}$ plays an essential role for the evaluation of $R^{(2)}$. We have also found that there are no qualitative differences in $R^{(2)}$ of the steady-state Boltzmann equation, the steady-state BGK equation and information theory, while $R^{(2,A)}$ also exhibits a slight deviation from each other. This deviation in $R^{(2,A)}$ would not be observed if we adopted $\phi^{(1)}$ of the steady-state Boltzmann equation for the lowest approximation of So-

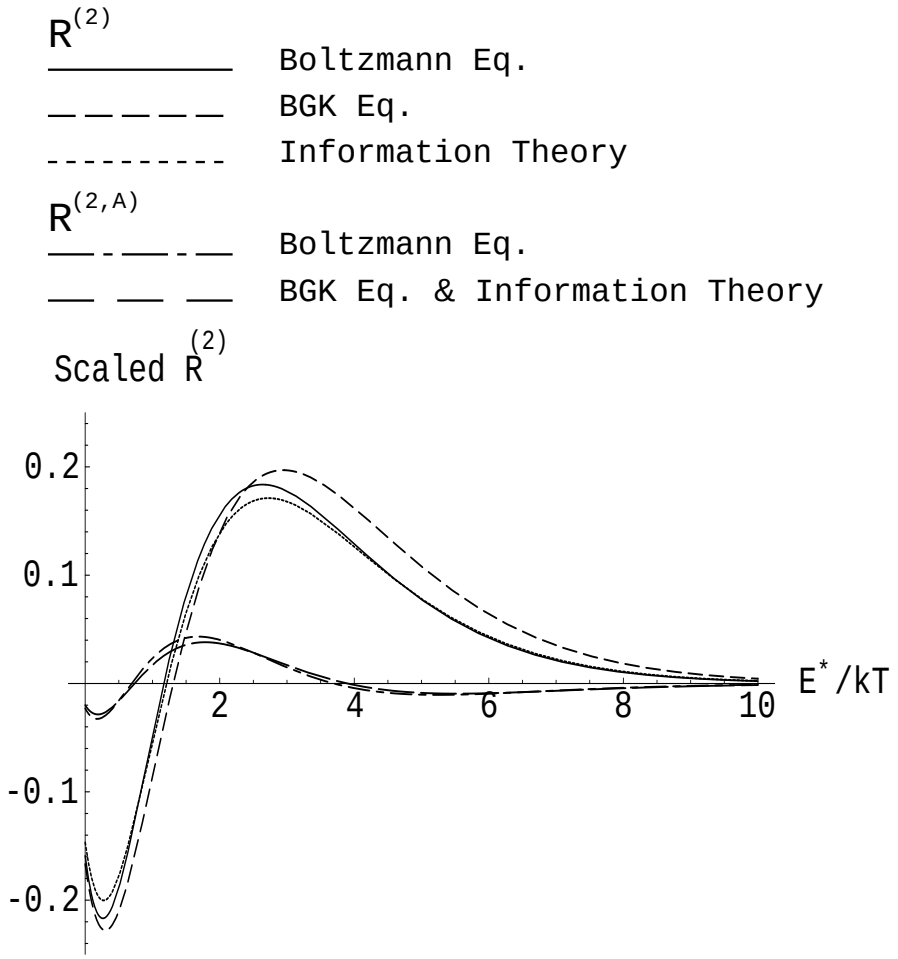

Figure 3.1: Scaled $R^{(2)}$ compared to scaled $R^{(2,A)}$ as a function of $E^*/\kappa T$ for the line-of-centers model.

nine polynomials as in the previous papers[101, 102]. This is because $\phi^{(1)}$ of the steady-state Boltzmann equation for the lowest Sonine approximation is identical with the precise $\phi^{(1)}$ of the steady-state BGK equation and information theory. It should be mentioned that we have found qualitative differences among these theories in some thermodynamic quantities, *e.g.* the second-order pressure tensor.[130, 147] The nonequilibrium effects on the rate of chemical reaction is an insensitive quantity to the differences among the three theories.

3.3 Discussion and Conclusion

The change of the rate of chemical reaction by the nonequilibrium flux can be interpreted as one of the local nonequilibrium effects, because it appears not to linear order of the heat flux but to nonlinear order of that. $\phi^{(2)}$ is indispensable for the calculation of the nonequilibrium effects on the rate of chemical reaction, since $R^{(1)}$ does not appear and $R^{(2,B)}$ is remarkably larger than $R^{(2,A)}$ as Fig.3.1 shows. This fact indicates the significance of the second-order coefficients in the solution of the steady-state Boltzmann equation as terms which reflect the local nonequilibrium effect. The nonequilibrium effect on the rate of chemical reaction will substantiate new significance of the second-order coefficients in the solution of the steady-state Boltzmann equation, although their importance has been demonstrated only for descriptions of shock wave profiles and sound propagation phenomena[10, 53, 54, 55, 56, 57, 58]. We note that the application of the second-order coefficients to shock wave and sound propagation does not require the explicit form of the second-order velocity distribution function. The nonequilibrium effects we consider appear mainly in the ranges of small $E^*/\kappa T$ where the chemical reaction often occurs, so that our results should be compared with experimental results in the early stage of the chemical reaction[87]; large additional effects due to density and temperature change of reactants become significant as the chemical reaction proceeds[104, 105].

We also propose a *thermometer* of a monatomic dilute gas system under steady heat flux. We mean that we can measure the temperature T around a heat bath at T_0 in the nonequilibrium steady-state system indirectly with the aid of the nonequilibrium effect on the rate of chemical reaction as follows. The nonequilibrium effect on the rate of chemical reaction in the early

stage around the heat bath can be measured. Thus, one can compare the experimental result with the theoretical result shown in Fig.3.1 with $T = T_0$. The difference between the former and the latter will indicate that the temperature T around the heat bath is not identical with T_0, that is, $T = T_0 + \Delta$. Here Δ should depend upon the heat flux in general. Substituting this temperature expression into the explicit expressions of $R^{(0)}$ in eq.(3.2), we obtain a new correction term

$$R^{(\mathrm{new})} = \frac{2n^2\sigma^2\Delta}{T_0}\left(\frac{\pi\kappa T_0}{m}\right)^{\frac{1}{2}}\left(1+\frac{2E^*}{\kappa T_0}\right)e^{-\frac{E^*}{\kappa T_0}}, \tag{3.8}$$

as the nonequilibrium effect on the rate of chemical reaction besides $R^{(2)}$ in Fig.3.1 with $T = T_0$. At last, we can estimate the gap Δ so as to make the new correction term match the experimental result. For example, if Δ in eq.(3.8) is proportional to the heat flux, we will confirm the relevancy of the slip effect[61, 148]. If Δ in eq.(3.8) is identical with $2mJ_x^2/5n^2\kappa^3T_0^2$, *i.e.* $1/T = 1/T_0 - 2mJ_x^2/5n^2\kappa^3T_0^4$, the experimental result will agree with the theoretical result from the steady-state Boltzmann equation with the *nonequilibrium temperature* $\theta = T_0$ predicted by Jou *et al.*[110] This indicates that the *nonequilibrium temperature* θ has an important physical meaning as the temperature which corresponds to that of the heat bath in the *local nonequilibrium state*. If not, the *nonequilibrium temperature* θ has no physical meaning in the *local nonequilibrium state* of simple dilute gases.

We show the comparison of the theoretical results, *i.e.* $R^{(2)}$ for the steady-state Boltzmann equation with $T = T_0$ and that with $\theta = T_0$, in Fig.3.2, where $R^{(2)}$ is scaled by $\pi^{1/2}d^2m^{1/2}J_x^2/\kappa^{5/2}T_0^{5/2}$. We note that one can obtain the explicit form of $R^{(2)}$ with $\theta = T_0$ expressed as the dashed line in Fig.3.2 as the sum of $R^{(2)}$ from eqs.(3.6) and (3.7) for the steady-state Boltzmann equation with $T = T_0$ and $R^{(\mathrm{new})}$ from eq.(3.8) with $\Delta = 2mJ_x^2/5n^2\kappa^3T_0^2$. We have found that there is a significant difference between $R^{(2)}$ with $T = T_0$ and that with $\theta = T_0$ for small $E^*/\kappa T_0$. This significant difference also appears in $R^{(2)}$ for the steady-state BGK equation and information theory. Similar difference in $R^{(2)}$ for information theory would also follow from the results of Fort and Cukrowski[100], although they were not interested in the ranges of small $E^*/\kappa T$. We emphasize that, however, our proposal written in this paragraph differs from that by Fort and Cukrowski[100] which uses a given value measured directly by a thermometer in order to determine T or θ regardless of the temperature of the heat bath.

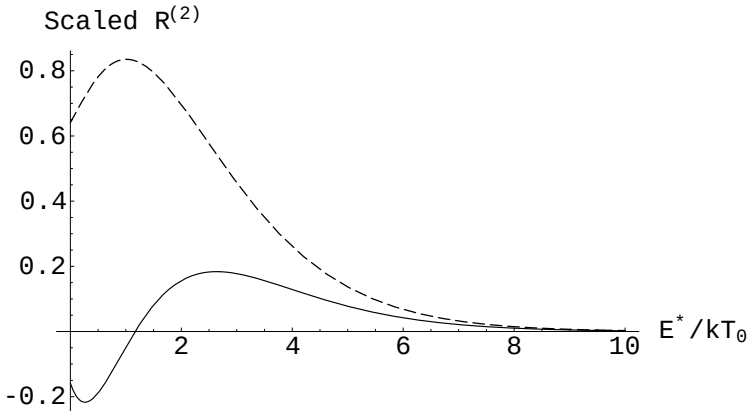

Figure 3.2: Comparison of scaled $R^{(2)}$ from the steady-state Boltzmann equation with $T = T_0$ (the solid line) and that with $\theta = T_0$ (the dashed line) as a function of $E^*/\kappa T_0$. Note that the former is identical with the result shown by the solid line in Fig.3.1 with $T = T_0$.

Chapter 4

Examination of Information Theory and Steady State Thermodynamics(SST) on the Boltzmann Equation

4.1 Information Theory

Let us introduce information theory proposed by Jou *et al.*.[110, 111, 112] Suppose a nonequilibrium system subject to a temperature gradient along the x-axis in a steady state whose velocity distribution function is expressed as $f = f(x, \mathbf{v})$. The Zubarev form for the nonequilibrium velocity distribution function under a heat flux can be obtained by maximizing the nonequilibrium entropy, defined as

$$S(x) \equiv -\kappa \int f \log f d\mathbf{v}, \tag{4.1}$$

under the constraints of the density:

$$n(x) \equiv \int f d\mathbf{v}, \tag{4.2}$$

and the temperature:

$$\frac{3n(x)\kappa T(x)}{2} \equiv \int \frac{m\mathbf{v}^2}{2} f d\mathbf{v}. \tag{4.3}$$

We assume no mean flow:

$$\int m\mathbf{v}f d\mathbf{v} = \mathbf{0}, \tag{4.4}$$

where $\mathbf{0}$ denotes the zero vector. Furthermore, we define the heat flux:

$$J_x \equiv \int \frac{m\mathbf{v}^2}{2} v_x f d\mathbf{v}. \tag{4.5}$$

It should be emphasized that the heat flux (4.5) is now *assumed* to be uniform as well as $n\kappa T$ by contrast with the case for the steady-state Boltzmann equation where its solubility conditions lead to the heat flux J_x being constant to second order.[59]

Jou *et al.* have finally obtained the nonequilibrium velocity distribution function to second order in the heat flux J_x by expanding the Zubarev's nonequilibrium velocity distribution function to second order as

$$f = \frac{1}{Z}\exp\left(-\beta\frac{m\mathbf{v}^2}{2}\right)\left[1 - \frac{4J_x}{5n\kappa T}\left(\frac{m}{2\kappa T}\right)^{\frac{1}{2}} c_x\left(\frac{5}{2\beta\kappa T} - \mathbf{c}^2\right) + \frac{4mJ_x^2}{25n^2\kappa^3T^3}c_x^2\left(\frac{5}{2\beta\kappa T} - \mathbf{c}^2\right)^2\right], \tag{4.6}$$

with the scaled velocity $\mathbf{c} \equiv (m/2\kappa T)^{1/2}\mathbf{v}$. Here Z is given by

$$Z = \frac{1}{n}\left(\frac{2\pi}{\beta m}\right)^{\frac{3}{2}}\left(1 + \frac{mJ_x^2}{5n^2\kappa^3T^3}\right), \tag{4.7}$$

in order to normalize f. The parameter β is found to be

$$\beta = \frac{1}{\kappa T}\left(1 + \frac{2mJ_x^2}{5n^2\kappa^3T^3}\right) \equiv \frac{1}{\kappa\theta}, \tag{4.8}$$

and has been used by Jou *et al.* in order to introduce θ as a *nonequilibrium temperature*. From eq.(4.8) it is clear that the *nonequilibrium temperature* θ is not identical with the temperature T defined in eq.(4.3), and θ is lower than T.[120]

By expanding the velocity distribution function (4.6) to second order in J_x, we obtain the expression for the *modified* velocity distribution function:

$$f = f^{(0)}\left\{1 - \frac{3J_x}{2n\kappa T}\left(\frac{\pi m}{2\kappa T}\right)^{\frac{1}{2}} c_x S^1_{\frac{3}{2}}(\mathbf{c}^2) + \frac{2mJ_x^2}{5n^2\kappa^3T^3}(1 - \mathbf{c}^2) + \frac{mJ_x^2}{5n^2\kappa^3T^3}c_x^2[3\sqrt{\pi}S^2_{\frac{1}{2}}(\mathbf{c}^2) + 2]\right\}, \tag{4.9}$$

where n and T have been identified in eqs.(4.2) and (4.3), respectively. This *modified* velocity distribution function has been also obtained and used by Fort and Cukrowski.[100] We have confirmed that the *modified* velocity distribution function still satisfies constraints (4.4) and (4.5), while the corrections appearing in eqs.(4.7) and (4.8) no longer appear in the density (4.2) and the temperature (4.3) with the *modified* velocity distribution function expressed in eq.(4.9). We adopt this *modified* velocity distribution function instead of the velocity distribution function shown in eq.(4.6) to calculate macroscopic quantities in this thesis. This adoption is based on the fact that the corrections in eqs.(4.7) and (4.8) are not significant, although Jou *et al.* believe that the correction appearing in eq.(4.8) has important physical meaning. (see also Sec.4.4) We mention that the first-order velocity distribution function for information theory in eq.(4.9) is identical with those for the steady-state Boltzmann equation for Maxwell molecules in eq.(2.41) and for the steady-state BGK equation in eq.(2.47), while those second-order velocity distribution functions are different from each other.

4.2 Nonlinear Nonequilibrium Thermodynamics

4.2.1 Extended Irreversible Thermodynamics(EIT)

Let us introduce one of the nonlinear nonequilibrium thermodynamics based on the local nonequilibrium hypothesis, extended irreversible thermodynamics(EIT) proposed by Jou *et al.*.[110, 111, 112] Note that all the notations below are valid only in this section.

EIT extends the Gibbs equation as

$$ds(\mathbf{r},t) = T^{-1}(\mathbf{r},t)d\epsilon(\mathbf{r},t) + T^{-1}(\mathbf{r},t)P(\mathbf{r},t)dv_e(\mathbf{r},t) - \alpha_e(\mathbf{r},t)\mathbf{j}(\mathbf{r},t)\cdot d\mathbf{j}(\mathbf{r},t), \tag{4.10}$$

where the nonequilibrium entropy per unit mass $s(\mathbf{r},t)$ is assumed as an additive quantity with $T(\mathbf{r},t)$ the temperature, $\epsilon(\mathbf{r},t)$ the inertial energy per unit mass, $P(\mathbf{r},t)$ the pressure, $v_e(\mathbf{r},t)$ volume per unit mass and $\mathbf{j}(\mathbf{r},t)$ the heat flux per unit mass. The heat flux is treated as an extensive thermodynamic variable in EIT. The explicit form of the coefficient α_e is determined

as follows. Equation (4.10) with the balance equations of energy and mass leads to an equation of time evolution of the nonequilibrium entropy,

$$n(\mathbf{r},t)\frac{\partial s(\mathbf{r},t)}{\partial t}+\nabla\cdot\left(\frac{\mathbf{j}(\mathbf{r},t)}{T(\mathbf{r},t)}\right) = \mathbf{j}(\mathbf{r},t)\cdot\left[\nabla\left(\frac{1}{T(\mathbf{r},t)}\right)-n(\mathbf{r},t)\alpha_e(\mathbf{r},t)\frac{\partial\mathbf{j}(\mathbf{r},t)}{\partial t}\right] > 0, \tag{4.11}$$

where $n(\mathbf{r},t)$ is the density and $\mathbf{j}(\mathbf{r},t)/T(\mathbf{r},t)$ represents an entropy flux, so that the left-hand side of eq.(4.11) corresponds to the production of the nonequilibrium entropy which must be always positive. In order to satisfy the positivity, one may assume

$$\mu_e(\mathbf{r},t)\mathbf{j}(\mathbf{r},t)=\nabla\left(\frac{1}{T(\mathbf{r},t)}\right)-n(\mathbf{r},t)\alpha_e(\mathbf{r},t)\frac{\partial\mathbf{j}(\mathbf{r},t)}{\partial t}. \tag{4.12}$$

The undetermined coefficient μ_e which must be positive is obtained as follows. Comparing eq.(4.12) with the relaxation law of heat flux called Maxwell-Cattaneo's law:

$$\tau_e(\mathbf{r},t)\frac{\partial\mathbf{j}(\mathbf{r},t)}{\partial t}+\mathbf{j}(\mathbf{r},t)=-\lambda_e(\mathbf{r},t)\nabla T(\mathbf{r},t), \tag{4.13}$$

one can obtain the explicit forms of α_e and μ_e as

$$\alpha_e(\mathbf{r},t)=\frac{\tau_e(\mathbf{r},t)}{n(\mathbf{r},t)\lambda_e(\mathbf{r},t)T^2(\mathbf{r},t)} \quad\text{and}\quad \mu_e(\mathbf{r},t)=\frac{1}{\lambda_e(\mathbf{r},t)T^2(\mathbf{r},t)}, \tag{4.14}$$

respectively. Here $\tau_e(\mathbf{r},t)$ represents a relaxation time, and $\lambda_e(\mathbf{r},t)$ denotes a thermal conductivity. Finally, the nonequilibrium entropy is determined explicitly as

$$s(\mathbf{r},t)=s_{eq}(\mathbf{r},t)-\frac{v_e(\mathbf{r},t)\tau_e(\mathbf{r},t)}{2\lambda_e(\mathbf{r},t)T^2(\mathbf{r},t)}\mathbf{j}(\mathbf{r},t)\cdot\mathbf{j}(\mathbf{r},t), \tag{4.15}$$

but this expression still contains the relaxation time $\tau_e(\mathbf{r},t)$ and the thermal conductivity $\lambda_e(\mathbf{r},t)$ which depends on the characteristics of microscopic materials and should be calculated from other microscopic theories. For example, if one adopt $\tau_e(\mathbf{r},t)=2m\lambda_e(\mathbf{r},t)/5n(\mathbf{r},t)\kappa^2T(\mathbf{r},t)$ from the steady-state BGK equation, the nonequilibrium entropy (4.15) agrees with that of information theory as will be shown in eq.(4.31). In EIT, the *nonequilibrium*

temperature and the *nonequilibrium pressure* are defined thermodynamically as

$$\frac{1}{\Theta(\mathbf{r},t)} \equiv \left(\frac{\partial s(\mathbf{r},t)}{\partial \epsilon(\mathbf{r},t)}\right)_{v,n,\mathbf{j}} \qquad \frac{\pi(\mathbf{r},t)}{\Theta(\mathbf{r},t)} \equiv \left(\frac{\partial s(\mathbf{r},t)}{\partial v_e(\mathbf{r},t)}\right)_{\epsilon,n,\mathbf{j}} \tag{4.16}$$

respectively. The nonequilibrium entropy (4.15) with $\tau_e(\mathbf{r},t) = 2m\lambda_e(\mathbf{r},t)/5n(\mathbf{r},t)\kappa^2 T(\mathbf{r},t)$ leads to the fact that the former is identical with the *nonequilibrium temperature* (4.8) from information theory, while the latter is not quantitatively but qualitatively the same as that predicted by information theory.[119]

4.2.2 Steady State Thermodynamics(SST)

We introduce another nonlinear nonequilibrium thermodynamics based on the local nonequilibrium hypothesis called steady-state thermodynamics(SST) which we will test in this thesis. Note that all the notations below are valid only in this section.

In SST, the nonequilibrium pressure $P(T, J|V, N)$ and the nonequilibrium chemical potential $\mu(T, J|V, N)$ are defined as

$$P(T, J|V, N) = -\frac{\partial F(T, J|V, N)}{\partial V} \quad \text{and} \quad \mu(T, J|V, N) = \frac{\partial F(T, J|V, N)}{\partial N}, \tag{4.17}$$

respectively. Here T the temperature of heat bath, J the heat flux, V the volume of nonequilibrium cell, N the number of particles in the nonequilibrium cell. SST assumes the existence of an additive thermodynamic potential $F(T, J|V, N)$, and that the heat flux J is the intensive thermodynamic variable. The additivity of $F(T, J|V, N)$ leads to the extended Euler equation:

$$F(T, J|V, N) = -VP(T, J|V, N) + N\mu(T, J|V, N). \tag{4.18}$$

SST has considered a nonequilibrium system in which an equilibrium cell and the nonequilibrium cell under steady heat conduction connected by an unmovable porous wall.(see Fig.2 in ref.[138]) In a steady state, SST has identified the chemical potential in the nonequilibrium cell with that in the equilibrium cell:

$$\mu(T, J|V, N) = \mu(T, 0|V', N'), \tag{4.19}$$

with V' the volume of equilibrium cell, N' the number of particles in the equilibrium cell.

The most important points in SST is that SST can make some predictions which can be examined by other microscopic theories. The first is that an order $\Psi(T, J|V, N)$ is caused by the heat flux:

$$\Psi(T, J|V, N) = -\frac{\partial F(T, J|V, N)}{\partial J}, \tag{4.20}$$

which depends on the direction of J, because $F(T, J|V, N)$ is an odd function of J.

The second is that the osmosis, defined as the difference between the pressure $P(T, J|V, N)$ of the nonequilibrium cell and the value $P(T, 0|V', N')$ of the equilibrium cell, namely

$$\Delta P \equiv P(T, J|V, N) - P(T, 0|V', N'), \tag{4.21}$$

always becomes positive, regardless of the direction of J. This prediction is made from the inequality,

$$\frac{\partial P(T, J|V, N)}{\partial J} = \frac{\Psi(T, J|V, N)}{V} > 0, \tag{4.22}$$

which is derived from eq.(4.18) with fixed $\mu(T, J|V, N)$ and eq.(4.20) with the fact that $F(T, J|V, N)$ is concave in intensive variables J. Note that $P(T, 0|V', N') = P(T, 0|V, N)$, and that $\mu(T, J|V, N)$ can be a constant since $\mu(T, 0|V', N')$ is constant when T and $P(T, 0|V', N')$ are fixed.

The third is that there is the following simple relation:

$$\frac{n_0}{n} = \frac{\partial P_0(T, J, P)}{\partial P}, \tag{4.23}$$

among the density n and the pressure $P(T, J|V, N)$ of the nonequilibrium cell, and the density n_0 and the pressure $P_0(T, J, P)$ of the equilibrium cell. Here we have changed the variables (T, V, N) in the equilibrium pressure $P(T, 0|V, N)$ to (T, J, P), and express it as $P_0(T, J, P)$. The relation (4.23) is derived as follows. The intensivity of the pressure is expressed as

$$P(T, J|V, N) = P(T, J|V/N, 1), \tag{4.24}$$

which leads to

$$\frac{\partial P(T,J|V,N)}{\partial N} = -\frac{V}{N}\frac{\partial P(T,J|V,N)}{\partial V}. \tag{4.25}$$

Additionally, from eq.(4.17), one can obtain

$$\frac{\partial P(T,J|V,N)}{\partial N} = -\frac{\partial \mu(T,J|V,N)}{\partial V}. \tag{4.26}$$

Using eq.(4.19), one can perform the following deformation

$$\frac{\partial \mu(T,J,P)}{\partial P} = \frac{\partial \mu(T,0,P_0(T,J,P))}{\partial P_0}\frac{\partial P_0(T,J,P)}{\partial P} \tag{4.27}$$

$$= \frac{1}{n_0}\frac{\partial P_0(T,J,P)}{\partial P}. \tag{4.28}$$

This equation with eqs.(4.25) and (4.26) results in the relation (4.23).

4.3 Examination

We examine both of information theory which corresponds to EIT and SST by the microscopic kinetic theory. Note that ET is not examined in this thesis, because ET does not predict any explicit forms of thermodynamic quantities such as the pressure tensor.

4.3.1 Test of Information Theory

Now the nonequilibrium velocity distribution functions to second order given in eqs.(4.9), (2.40) and (2.41) shall be applied to the nonequilibrium steady-state system. We note that we adopt only the result in eq.(2.40) for 7th Sonine approximation in this section. All the definitions of physical quantities in this thesis are the same as those in Sec. 2.5.

To begin with, the pressure tensor in the nonequilibrium steady state P_{ij} becomes

$$P_{ij} = n\kappa T\left[\delta_{ij} + \lambda_P^{ij}\frac{mJ_x^2}{n^2\kappa^3 T^3}\right], \tag{4.29}$$

with the unit tensor δ_{ij} and the numerical tensor components λ_P^{ij} shown in Table 4.1. Note that the off-diagonal components of λ_P^{ij} are zero and that $\lambda_P^{yy} = \lambda_P^{zz}$ is satisfied. We have found that λ_P^{ij} for information theory is qualitatively different from those for the steady-state Boltzmann equation for both hard-core and Maxwell molecules: P_{xx} becomes larger than P_{yy} and P_{zz} for information theory[119, 121], while P_{xx} becomes smaller than P_{yy} and P_{zz} for the steady-state Boltzmann equation for hard-core molecules, and no second-order corrections appear in P_{ij} for the steady-state Boltzmann equation for Maxwell molecules.

Table 4.1: The numerical constants for the macroscopic quantities: the precise values for information theory, the 7th Sonine approximation values for hard-core molecules and the exact values for Maxwell molecules.

	λ_P^{xx}	λ_P^{yy}	λ_S
information	$\frac{12}{25}$	$-\frac{6}{25}$	$-\frac{1}{5}$
hard-core	-4.600×10^{-2}	2.300×10^{-2}	-2.035×10^{-1}
Maxwell	0	0	$-\frac{1}{5}$

Each component of the kinetic temperature in the nonequilibrium steady state, i.e. $T_{\rm i}$ for i = x, y and z is also calculated as

$$T_{\rm i} = T[1 + \lambda_P^{\rm ii} \frac{m J_x^2}{n^2 \kappa^3 T^3}], \tag{4.30}$$

for i = x, y and z. Numerical values for the constants in the second-order term $\lambda_P^{\rm ii}$ are the same as $\lambda_P^{\rm ij}$ for i = j given in Table 4.1. It is found that T_x becomes larger than T_y and T_z for information theory, while T_x becomes smaller than T_y and T_z for the steady-state Boltzmann equation for hard-core molecules, and no corrections appear in $T_{\rm i}$ for the steady-state Boltzmann equation for Maxwell molecules.

The Shannon entropy in the nonequilibrium steady state becomes

$$S(x) = -n\kappa \log \left[n \left(\frac{m}{2\pi\kappa T} \right)^{\frac{3}{2}} \right] + \frac{3}{2} n\kappa + \lambda_S \frac{m J_x^2}{n\kappa^2 T^3}, \tag{4.31}$$

to second order with $\lambda_S = -1/5$ for information theory and for the steady-state Boltzmann equation for Maxwell molecules. (see Table 4.1) It is found

that λ_S calculated from the steady-state Boltzmann equation for hard-core molecules slightly deviates from the others. This is because the correction term for the Shannon entropy is determined only by the first-order velocity distribution function, as was indicated in ref.[110].

4.3.2 Test of Steady State Thermodynamics(SST)

Let us introduce a simple nonequilibrium steady-state system shown in Fig.4.1. The cell on the left-hand side is at equilibrium at temperature T_0. The cell on the right-hand side is in a nonequilibrium state under a temperature gradient along the x-axis caused by the right wall (at $x = L_0$) at temperature T_1 and the thin mid-wall (at $x = 0$) at temperature T_0, of thickness less than or equal to the mean free path l of the dilute gases. Both cells are filled with dilute gases and connected by a small hole of diameter d_h on the thin mid-wall. The diameter of the small hole d_h is much smaller than l, i.e. $d_h \ll l$. Molecules which have passed through the small hole are relaxed into the state of the cell they go into after a few interactions, so that they do not affect the macroscopic state of that cell.

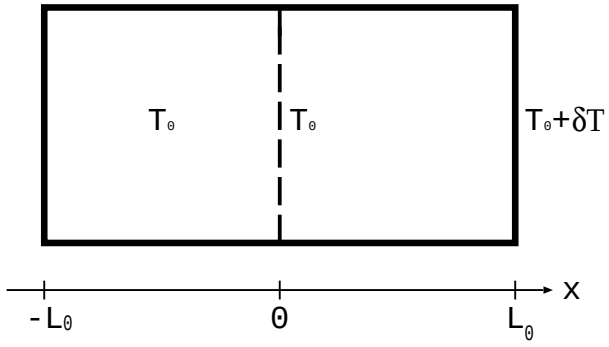

Figure 4.1: A simple nonequilibrium steady-state system. The mean mass flux at the small hole is zero in the nonequilibrium steady state.

This system is inspired by SST suggested by Sasa and Tasaki.[138] We examine SST in this system from the microscopic viewpoint, that is, by applying the velocity distribution function for the steady-state Boltzmann equation for both hard-core molecules and Maxwell molecules to the cell on the right-hand side in the system illustrated in Fig.4.1. We also use the

velocity distribution function for the steady-state BGK equation to second order in the test of SST.

SST predicted the following results. When the system shown in Fig.4.1 is in a steady-state, the osmosis, defined as the difference between the pressure P_{xx} of the cell in the nonequilibrium steady state and the value P_0 of the cell at equilibrium, namely

$$\Delta P \equiv P_{xx} - P_0, \tag{4.32}$$

always becomes positive. (see eq.(4.21)) Additionally, there is a relation

$$\frac{n(0)}{n_0} = \left(\frac{\partial P_{xx}}{\partial P_0}\right)_{T_0, J_x}, \tag{4.33}$$

connecting $n(0)$, P_{xx}, n_0 and P_0, where $n(0)$ is the density of the cell in the nonequilibrium steady state around the hole and n_0 is that of the cell at equilibrium. (see eq.(4.23))

We consider the nonequilibrium steady-state where the mean mass flux at the hole is zero:

$$\int_0^\infty \mathrm{d}c_x \int_{-\infty}^\infty \mathrm{d}^2 c_\perp m c_x f_0 + \int_{-\infty}^0 \mathrm{d}c_x \int_{-\infty}^\infty \mathrm{d}^2 c_\perp m c_x f|_{x=0} = 0, \tag{4.34}$$

where $c_\perp$ represents the components of the velocity which are orthogonal to c_x, i.e. c_y and c_z. Note that we consider the mean mass flux at the hole, so that we put $x = 0$ in f. $f_0 = n_0(m/2\pi\kappa T_0)^{3/2} e^{-m\mathbf{v}^2/2\kappa T_0}$ is the velocity distribution function of the cell on the left-hand side at equilibrium at temperature T_0 and density n_0. From eq.(4.34), the relation between $n(0)$ and n_0 is obtained as

$$n(0) = n_0[1 + \lambda_n \frac{m J_x^2}{n_0^2 \kappa^3 T_0^3}], \tag{4.35}$$

to second order. The value for the constant λ_n is given in Table 4.2. The density of the cell in the nonequilibrium steady state around the hole $n(0)$ is greater than that of the cell at equilibrium n_0 regardless of the sign of J_x. We emphasize that λ_n could not be calculated if we did not derive the explicit form of the velocity distribution function f to second order. We have adopted the boundary condition around the hole, $T(0) = T_0$, in order to examine SST.

Although it is believed that the Knudsen layer effect, i.e. the slip effect is dominant around the 'wall'[5, 26, 61], for reasons of simplification, we do not consider the slip effect around the 'hole' in this paper. If the slip effect is not dominant, the density of the cell in the nonequilibrium steady state will always be larger than that of the cell at equilibrium, regardless of the sign of J_x. This can be tested by experiments on the nonequilibrium steady-state system shown in Fig.4.1.

We also calculate the osmosis ΔP in eq.(4.32) as

$$\Delta P = \lambda_{\Delta P} \frac{m J_x^2}{n_0 \kappa^2 T_0^2}, \tag{4.36}$$

to second order, using eqs.(2.50), (4.35) and $P_0 = n_0 \kappa T_0$. Values for $\lambda_{\Delta P}$ are given in Table 4.2. We have found that $\lambda_{\Delta P}$ is always positive, which agrees with the prediction by SST[138].

Table 4.2: Numerical constants for the macroscopic quantities: the ith approximation quantities for hard-core molecules and the exact values for Maxwell molecules and the steady-state BGK equation. The values of λ_n, $\lambda_{\Delta P}$ and λ_{J^*} for hard-core molecules has not yet converged to 4th approximation b_{0r} and b_{2r} values. The ratios of the 7th to the 6th approximation λ_n, $\lambda_{\Delta P}$ and λ_{J^*} are 1.011, 1.023 and 1.004, respectively, so that the errors included in the 7th approximation λ_n, $\lambda_{\Delta P}$ and λ_{J^*} appear to be less than about one or two percent. Note that $n(0) = n_0$ to first order, and that osmosis does not appear to first order.

ith	λ_n	$\lambda_{\Delta P}$	λ_{J^*}
4th	9.255×10^{-2}	4.608×10^{-2}	-3.237×10^{-1}
5th	8.528×10^{-2}	3.917×10^{-2}	-3.109×10^{-1}
6th	8.296×10^{-2}	3.694×10^{-2}	-3.073×10^{-1}
7th	8.210×10^{-2}	3.609×10^{-2}	-3.060×10^{-1}
Maxwell	$\frac{71}{1575}$	$\frac{71}{1575}$	$-\frac{41}{105}$
BGK equation	$\frac{2}{25}$	$\frac{2}{25}$	$-\frac{11}{50}$

Furthermore, we are able to test the relation (4.33). Though substitution of eqs.(2.50) and (4.35) into eq.(4.33) leads to the relation $\lambda_P^{xx}/\lambda_n = -2$,

our numerical results conflict with this relation: our results give $\lambda_P^{xx}/\lambda_n = -0.5604$ for 7th approximation b_{0r} and b_{2r} for hard-core molecules and $\lambda_P^{xx}/\lambda_n = 0$ for both Maxwell molecules and the steady-state BGK equation. We have also confirmed that the relation $\lambda_P^{xx}/\lambda_n = -2$ predicted in SST[138] is not modified if the boundary condition around the hole can be written in the form:

$$T(0) = T_0[1 + \lambda_T \frac{m J_x^2}{n_0^2 \kappa^3 T_0^3}], \tag{4.37}$$

where the constant λ_T represents the difference between the temperature of molecules around the hole and that of the mid-wall. Our boundary condition $T(0) = T_0$ corresponds to putting $\lambda_T = 0$ for any kinetic models. It can be concluded that, although we regard a state in which the mean mass flux at the hole is zero to be a nonequilibrium steady state, as in eq.(4.34), this state has yet to be interpreted phenomenologically.

On the other hand, by virtue of the derivation of the explicit form of the velocity distribution function f to second order, we can also calculate the x component of the heat flux at the hole as

$$\begin{aligned} J^* &\equiv \left(\frac{2\kappa T}{m}\right)^3 \int_0^\infty \mathrm{d}c_x \int_{-\infty}^\infty \mathrm{d}^2 c_\perp \frac{m\mathbf{c}^2}{2} c_x f_0 + \left(\frac{2\kappa T}{m}\right)^3 \int_{-\infty}^0 \mathrm{d}c_x \int_{-\infty}^\infty \mathrm{d}^2 c_\perp \frac{m\mathbf{c}^2}{2} c_x f|_{x=0} \\ &= \frac{J_x}{2} + \lambda_{J^*} \frac{m J_x^2}{n_0 \kappa^2 T_0^2} \left(\frac{2\kappa T_0}{\pi m}\right)^{\frac{1}{2}}, \end{aligned} \tag{4.38}$$

to second order using eq.(4.35). Numerical values for the constant λ_{J^*} are given in Table 4.2. The first-order term on the right-hand side of eq.(4.38) is from Fourier's law, while the second-order term also appears on the right-hand side of eq.(4.38), though the second-order heat flux $\mathbf{J}^{(2)}$ does not exist in the cell in the nonequilibrium steady state. This fact indicates that $T(0)$ is not appropriate for the *nonequilibrium temperature*, if J^* suggests the existence of the *nonequilibrium temperature*.

4.4 Discussion and Conclusion

It is seen that the first-order velocity distribution functions for the steady-state Boltzmann equation for both hard-core and Maxwell molecules, i.e.

the first-order terms in eqs.(2.40) and (2.41), are consistent with that derived by expanding Zubarev's velocity distribution function[33, 116, 117]. This consistency is attributed to the fact that a nonequilibrium correction in the nonequilibrium entropy should appear to even order of a nonequilibrium flux, *e.g.* $\delta S \propto -J_x^2$, in order that the nonequilibrium entropy has a maximum at $J_x = 0$, and that a thermodynamic force $F = \partial \delta S / \partial J_x$ which drives a nonequilibrium system towards the state of equilibrium is proportional to the nonequilibrium flux.[44] This fact leads to a conclusion that the nonequilibrium entropy is not modified from the local equilibrium entropy to first order, and that the Shannon-type entropy is appropriate as the nonequilibrium entropy to first order.

On the other hand, we have confirmed that both forms (2.40) and (2.41) of the second-order velocity distribution functions differ from that suggested by information theory. Although Jou *et al.* have applied information theory to nonequilibrium dilute gases[60, 100, 118, 119, 120, 121, 122], we have found that information theory contradicts the steady-state Boltzmann equation: all the macroscopic quantities for information theory except for the Shannon entropy S in eq.(4.31) are qualitatively different from those for the steady-state Boltzmann equation for both hard-core and Maxwell molecules. These qualitative differences between information theory and the steady-state Boltzmann equation still appear no matter which boundary condition is adopted. It is conjectured that the entropy defined in eq.(4.1) is not appropriate as the nonequilibrium entropy to second order, though the Shannon-type entropy has been widely used as the nonequilibrium entropy to any order[33, 44, 107, 108, 109, 110, 112, 116, 117, 128, 129, 149]; some nonequilibrium corrections dependent on microscopic models are necessary for the nonequilibrium entropy to second order. We emphasize that it is probably the first time to find qualitative differences between information theory and nonequilibrium microscopic theories and demonstrate that information theory is inconsistent with the nonequilibrium microscopic theories. It can be also stated that EIT which corresponds to information theory also conflicts with the microscopic kinetic theory. We conclude that, although many statistical physicists have believed the existence of a universal nonequilibrium velocity distribution function in the nonequilibrium steady state by maximizing the Shannon-type entropy[33, 44, 107, 108, 109, 110, 112, 116, 117, 128, 129, 149], the universal nonlinear nonequilibrium velocity distribution function does not exist in the nonequilibrium steady state. It is also worth

mentioning that, although information theory based on the Tsallis entropy has been also developed[150, 151], the general form of the velocity distribution function cannot be expanded even to first order because the expanded velocity distribution function diverges.

We have also confirmed that, in all the macroscopic quantities calculated in the present thesis, there are no differences between the results from the *modified* velocity distribution function given in eq.(4.9) and those from Jou's velocity distribution function shown in eq.(4.6) so long as the same boundary condition is adopted. This suggests that the *nonequilibrium temperature* θ has no physical significance in the phenomena treated in this thesis, except if θ corresponds to the temperature of a heat bath at boundary. We emphasize that the identifications of the density, the temperature and the mean flow (see eqs.(2.10), (2.11) and (2.12)) do not affect the physical properties of the velocity distribution function for the steady-state Boltzmann equation[59], and that those identifications must be satisfied for the conservation laws in the case for the steady-state BGK equation.[66, 67]

All the values of our results in this thesis can be determined by specifying the boundary condition $T(0)$, whether $T(0) = T_0$ or not. Therefore, as was discussed in Sec.3.3, a nonequilibrium temperature which does not correspond to T_0 has no physical meaning in simple nonequilibrium dilute gas systems. In other nonequilibrium phenomena such as sound propagation[121], radiations[123, 124, 125, 126, 127] and sheared glasses[152], "nonequilibrium temperature"s defined by different ways may exist, but they might depend on properties of the phenomena and may not be universal. In fact, it is thought that the "nonequilibrium temperature" for sheared glasses appears because of separated multiple time scales which simple nonequilibrium dilute gas systems do not possess.

The discrepancy between SST and the microscopic kinetic theories leads to the following possibilities.

(1) The type of connection between both cells as in eq.(4.34) may not correspond to the relation shown in eq.(4.19).

(2) The order $\Psi(T, J|V, N)$ in eq.(4.20) caused by the heat flux J in the *local nonequilibrium state* may be proportional not to J but to J^2.

(3) Because the temperature profile becomes definitely nonlinear

as the heat flux becomes larger(see eq.(2.49)), the assumption of uniform additivity may break down.

(1) is indicated by Sasa and Tasaki and most possible. The connection (4.34) has yet to be interpreted phenomenologically. We think (2) is also crucial. No order proportional to J has been found through all the nonequilibrium phenomena considered in this thesis. On the other hand, the order proportional to J^2 has been detected in the anisotropic pressure (2.50) and the anisotropic kinetic temperature (2.52). This nonlinear anisotropism means that motions of molecules along the heat flux become ordered not linearly but nonlinearly, which is never obtained in SST.

(3) is also applicable to ET and EIT. (3) means that a thin system in the *local nonequilibrium state* without any macroscopically observable changes cannot be obtained by arbitrary splitting of a nonequilibrium steady-state system. We emphasize that the characteristic length where the macroscopic observables such as the temperature can be constant changes and has a correlation along the nonlinear temperature profile. Therefore, for the case of the *local nonequilibrium state* with the nonlinear temperature profile, at least uniform additivity breaks down and another proper additivity may be needed even in non-correlated dilute gas systems. We also propose that, even in the *local nonequilibrium state*, the uniform additivity holds for the case of special molecules which reproduce a linear temperature profile, that is, eq.(2.49) with $\varphi = 0$.

At least in three dimension, the long-range and long-time correlations appearing in linear transport phenomena of dense gas does not disturb fluid dynamics and the uniform additivity, which assures the existence of the linear nonequilibrium thermodynamics based on the local equilibrium hypothesis. However, in a "bounded" dilute gas system, spatial correlation of fluctuations of conservation quantities under linear temperature profile does not disappear through the entire system.[153, 154] Of course, at least in the thermodynamic limit system, the spatial correlation should disappear and restore the local equilibrium state. However, for the case of nonlinear temperature profile, such the system size spatial correlation of thermodynamic fluctuations might appear even in the thermodynamic limit, because the nonlinear temperature profile would cause the further correlation which we have suggested in the previous paragraph. The existence of such the spatial correlation means the breakdown of the uniform additivity.

Chapter 5

Summary

5.1 Kinetic Theory

The velocity distribution function of the steady-state Boltzmann equation for hard-core molecules subject to a temperature gradient has been derived explicitly to second order in the temperature gradient, as was shown explicitly in eq.(2.40) and graphically in Fig.2.3. The validity and the efficiency of our second-order solution has been demonstrated by Fushiki's numerical experiment. It can be concluded that the assumption of molecular chaos and the Boltzmann equation are valid so long as the scale separation $d \ll l \ll L$ holds. We believe that the second-order solution of the steady-state Boltzmann equation which produces nonlinear nonequilibrium phenomena reflects the local nonequilibrium effect.

In the nonequilibrium transport phenomena of gases which reflect the *local nonequilibrium state*, we have found qualitative differences between hard-core molecules and Maxwell molecules in the pressure tensor (2.50) and the kinetic temperature (2.52). The qualitative differences between hard-core molecules and Maxwell molecules still appear no matter which boundary condition is adopted. This qualitative difference is attributed to the special nature of Maxwell molecules that the collision frequency is independent of the magnitude of the relative velocity g. Therefore, it appears that, in the *local nonequilibrium state*, Maxwell molecules do not possess the characteristics of other models of molecules which interact with each other by other central forces.

We have also demonstrated that the steady-state BGK equation belongs to the same universality class as Maxwell molecules, and that it does not capture the essence of hard-core molecules. The qualitative agreements between the steady-state BGK equation and Maxwell molecules are due to the fact that g-dependency cannot be absorbed in the single relaxation time of the BGK equation. We conclude that microscopic models which possess the following properties could not be applied to describe the *local nonequilibrium state*.

(1) Collision frequency of particles does not depend on g.

(2) Relaxation to local equilibrium state is described only by a single relaxation time.

We can conclude that any universal nonlinear nonequilibrium velocity distribution function does not seem to exist, even when the velocity distribution function is expressed only in terms of macroscopic quantities. In fact, as mentioned above, we have detected the significant qualitative differences in the thermodynamic quantities dependent on the microscopic kinetic models. These results indicate that the characteristics of microscopic models appear in the *local nonequilibrium state* and affect even qualitatively the macroscopic quantities.

5.2 Chemical Reaction

The second-order solution of the steady-state Boltzmann equation for hard-core molecules is indispensable for the calculation of the nonequilibrium effects on the rate of chemical reaction. This indicates the significance of the second-order coefficients as terms which reflect the local nonequilibrium effect. The nonequilibrium effect on the rate of chemical reaction will substantiate new significance of the second-order coefficients, besides descriptions of shock wave profiles and sound propagation phenomena. We have also compared our result with those from the steady-state BGK equation and information theory, and confirmed no qualitative differences among them.

We also suggest a *thermometer* of a monatomic dilute gas system under steady heat flux: one can measure the kinetic temperature around a heat bath in the nonequilibrium steady-state system indirectly with the aid of

the nonequilibrium effect on the rate of chemical reaction. We have found that there is a significant difference between $R^{(2)}$ with $T = T_0$ and that with $\theta = T_0$. The latter case indicates that the *nonequilibrium temperature* θ has an important physical meaning as the temperature which corresponds to the temperature of the heat bath, otherwise θ has no physical meaning in the *local nonequilibrium state* of simple dilute gases.

5.3 Nonlinear Nonequilibrium Statistical Mechanics and Thermodynamics

The first-order velocity distribution functions for the steady-state Boltzmann equation for both hard-core and Maxwell molecules are consistent with that derived by expanding Zubarev's velocity distribution function. This consistency is attributed to the fact that a nonequilibrium correction in the nonequilibrium entropy should appear to second order of a nonequilibrium flux, and that the Shannon-type entropy is appropriate as the nonequilibrium entropy to first order.

On the other hand, we have confirmed that both forms (2.40) and (2.41) of the second-order velocity distribution functions differ from that suggested by information theory. Although Jou *et al.* have applied information theory to nonequilibrium dilute gases, we have found that information theory contradicts the steady-state Boltzmann equation. The qualitative differences between information theory and the steady-state Boltzmann equation still appear no matter which boundary condition is adopted. We suggest that the entropy defined in eq.(4.1) is not appropriate as the nonequilibrium entropy to second order, and that some nonequilibrium corrections dependent on microscopic models are needed for the nonequilibrium entropy to second order. It can be concluded that, though quite a few statistical physicists have believed the existence of a universal velocity distribution function in the nonequilibrium steady state by maximizing the Shannon-type entropy, the universal nonlinear nonequilibrium velocity distribution function does not exist in the *local nonequilibrium state*.

We have found that, in the simple nonequilibrium steady-state system, SST conflicts with the steady-state Boltzmann equation and the steady-state BGK equation. We have considered the grounds for the discrepancy between

SST and the microscopic kinetic theories , and concluded that, for the case of the *local nonequilibrium state* with the nonlinear temperature profile, at least uniform additivity breaks down, and that another proper additivity may be needed even in non-correlated dilute gas systems. This conclusion is also applicable to ET and EIT.

Chapter 6

Future Perspectives of Nonequilibrium Statistical Physics

The present thesis does not discuss any boundary problems as was mentioned in Sec.4.3.2. Those problems are physically important in nonequilibrium transport phenomena of gases, because all the values of thermodynamic quantities can be determined by specifying the boundary conditions. Previous studies on the boundary effects have reported that, under nonequilibrium heat conduction, there is a difference between the temperature of a heat bath wall and the kinetic temperature of gases in the system. They have also believed that the temperature gap called "temperature slip" is proportional to the heat flux in the system of gases. However, almost all those studies have assumed the following interaction rules between the heat bath wall and gas molecules.

(i) Diffusive reflection : once a molecule collide with a heat bath wall, the molecule is distributed at the wall by an equilibrium velocity distribution function at the temperature of the heat bath wall.

(ii) Elastic reflection : once a molecule collide with a heat bath wall, the molecule is reflected elastically on the wall surface.

(iii) Maxwell reflection: once molecules collide with a heat bath

wall, some of the molecules are distributed by the rule (i), while the other of them are reflected by the rule (ii) on the wall surface.

The rule (i) is based on the speculations that a state inside the heat bath wall must be perfectly equilibrium even when the system of gases is in any nonequilibrium states, while this speculation has not been confirmed yet. The rule (ii) implicitly assumes that a reflection rule has been already determined regardless of a state inside the heat bath wall. The rule (iii) is used most often in the previous works, because one can fit the theoretical results to numerical results by determining the mixing rate of the two rules (i) and (ii).

However, the validity of the reflection rules mentioned above has not been confirmed yet, especially in the *local nonequilibrium state* under heat conduction. We believe that it is necessary to investigate the boundary effect without the reflection rules. This is because we suppose that, when the system of gases is in the *local nonequilibrium state*, the heat bath wall may not be in a perfectly equilibrium state, and that the reflection rule of the gases on it may be affected by the state of the heat bath wall. We also conjecture that, in that case, there may be a thin transition regime in the wall surface where the state of the wall compositions changes from the *local nonequilibrium state* to the perfectly equilibrium one along the depth from its surface. In the near future, we will perform a numerical experiment without any reflection hypotheses such as (i)-(iii) on the heat bath wall.

On the other hand, the author conceive that a chemical reaction inside a biochemical molecule such as a protein is interesting from the viewpoint of the nonequilibrium statistical physics of *local nonequilibrium states*. It has been reported that strong heat fluxes flow inside the protein molecule when the molecule is in the reaction. Such the chemical reaction phenomena cannot be described by the nonequilibrium statistical mechanics or the nonequilibrium thermodynamics based on the local equilibrium hypothesis. These previous reports make the author believe that the strong heat fluxes inside the reacting protein essentially operate the processes and the rates of the reactions, and that the local nonequilibrium effects play an essential role also in such the *small* nonequilibrium system as the reacting protein. For a usual large nonequilibrium system such as a nonequilibrium gas system under a heat flux, we have already found that the macroscopic heat flux affects the rate of chemical reaction of gases, and that the second-order solution of

the Boltzmann equation which reflects the local nonequilibrium effect plays an essential role for estimating it. The author trusts the significance, the necessity and the possibility of constructing the nonequilibrium statistical mechanics and thermodynamics of the *local nonequilibrium state* through the small and strongly nonequilibrium system such as the reacting protein molecule.

Appendix A

Calculation of Ω_{kr}

From the definition of Q_{kr}, Ω_{kr} can be calculated using the mathematical properties of the spherical harmonic functions and Sonine polynomials.[25, 26] For example, $c_{1x}Q_{kr}$ can be rewritten as

$$\left(\frac{2\kappa T}{m}\right)^{\frac{1}{2}} c_{1x}Q_{kr} = \frac{\sqrt{\pi}}{2}(\frac{m}{2\kappa T})^{\frac{k}{2}} S^r_{k+\frac{1}{2}}(\mathbf{c}_1^2)[Y^{(1)}_{k+1}(\mathbf{c}_1) - \frac{2\kappa T}{m}c_1^2 Y^{(1)}_{k-1}(\mathbf{c}_1)], \quad \text{(A.1)}$$

using the recurrence formula[155]:

$$(2k+1)\left(\frac{2\kappa T}{m}\right)^{\frac{1}{2}} c_{1x}Y_k(\mathbf{c}_1) = Y^{(1)}_{k+1}(\mathbf{c}_1) - \frac{2\kappa T}{m}c_1^2 Y^{(1)}_{k-1}(\mathbf{c}_1). \quad \text{(A.2)}$$

Integrating eq.(A.1) over $(2\kappa T/m)^{1/2}\mathbf{c}_1$ with f_1 from eq.(2.13) can be performed by using the orthogonality properties of the spherical harmonic functions and Sonine polynomials such as

$$\int_0^\infty X^k e^{-X} S^p_k(X) S^q_k(X) dX = \frac{\delta_{p,q}}{\Gamma(p+k+1)p!}, \quad \text{(A.3)}$$

with the Kronecker delta $\delta_{p,q}$,

$$\int_0^\infty X^{k+\frac{3}{2}} e^{-X} S^p_{k+\frac{1}{2}}(X) S^q_{k+\frac{3}{2}}(X) dX = \frac{(-1)^{p-q}}{\Gamma(p+k+\frac{3}{2})q!}, \quad \text{(A.4)}$$

for $p = q$ and $p = q+1$, and is zero otherwise, and

$$\int_{-1}^{1} P^{(p)}_m(X) P^{(p)}_n(X) dX = \frac{2\delta_{m,n}}{2m+1}\frac{(m+p)!}{(m-p)!}. \quad \text{(A.5)}$$

(see refs.[25, 26, 155]) Finally, we can calculate $D_{k,r}$, $E_{k,r}$ and $G_{k,r}$ defined as

$$D_{k,r} \equiv \frac{1}{n}\overline{c_{1x}Q_{kr}}, \quad E_{k,r} \equiv \frac{1}{n}\overline{c_{1y}Q_{kr}} \quad \text{and} \quad G_{k,r} \equiv \frac{1}{n}\overline{c_{1z}Q_{kr}}. \tag{A.6}$$

The results can be written as

$$D_{k,r} = \frac{1}{2k+3}\{(k+r+\frac{3}{2})B^{(1)}_{k+1,r} - B^{(1)}_{k+1,r-1}\} - \frac{1}{2k-1}\{B^{(1)}_{k-1,r} - (r+1)B^{(1)}_{k-1,r+1}\}, \tag{A.7}$$

and

$$E_{k,r} = \frac{1}{2k+3}\{(k+r+\frac{3}{2})C^{(1)}_{k+1,r} - C^{(1)}_{k+1,r-1}\} - \frac{1}{2k-1}\{C^{(1)}_{k-1,r} - (r+1)C^{(1)}_{k-1,r+1}\}, \tag{A.8}$$

and

$$G_{k,r} = \frac{k+1}{2k+3}\{(k+r+\frac{3}{2})B_{k+1,r} - B_{k+1,r-1}\} + \frac{k}{2k-1}\{B_{k-1,r} - (r+1)B_{k-1,r+1}\}. \tag{A.9}$$

Additionally, $c_{1x}\partial_x Q_{kr}$ can be rewritten as

$$c_{1x}\partial_x Q_{kr} = -(k+\frac{1}{2})\sqrt{\pi}(\frac{m}{2\kappa T})^{\frac{k}{2}}\frac{\partial_x T}{T}c_{1x}Y_k(\mathbf{c}_1)[(r+\frac{k}{2})S^r_{k+\frac{1}{2}}(\mathbf{c}_1^2) - S^{r-1}_{k+\frac{1}{2}}(\mathbf{c}_1^2)], \tag{A.10}$$

using the formulae[155]:

$$\partial_X S^p_k(X) = -S^{p-1}_{k+1}(X), \tag{A.11}$$

and

$$XS^{p-1}_{k+\frac{3}{2}}(X) = S^{p-1}_{k+\frac{1}{2}}(X) - pS^p_{k+\frac{1}{2}}(X). \tag{A.12}$$

Therefore, by integrating eq.(A.10) over $(2\kappa T/m)^{1/2}\mathbf{c}_1$, with f_1 from eq.(2.13), it is found that

$$\overline{c_{1x}\partial_x Q_{kr}} = -n\frac{\partial_x T}{T}\{(r+\frac{k}{2})D_{k,r} - D_{k,r-1}\}. \tag{A.13}$$

Similarly $\overline{c_{1y}\partial_y Q_{kr}}$ and $\overline{c_{1z}\partial_z Q_{kr}}$ are obtained by replacing the differential coefficients with respect to x by the corresponding differential coefficients with respect to y and z, the $D_{k,r}$'s by the corresponding $E_{k,r}$'s and $G_{k,r}$'s, respectively. Substituting these results into eq.(2.23), Ω_{kr} finally becomes eq.(2.25).

Appendix B

Details of $F^1_{kr}(\chi)$

The details of $F^1_{kr}(\chi)$ are as follows. Substituting the general forms of f_1, f_2 in eq.(2.13) and Q'_{kr} in eq.(2.21) into $F^1_{kr}(\chi)$ in eq.(2.28), $F^1_{kr}(\chi)$ can be written as[25]

$$F^1_{kr}(\chi) = \sum_{n_1,n_2,k_1,k_2,k_1\geq p_1\geq 0,k_2\geq p_2\geq 0} W^{n_1,n_2,p_1,p_2}_{k,k_1,k_2}\Xi^{r,n_1,n_2,p_1,p_2}_{k,k_1,k_2}(\chi), \qquad \text{(B.1)}$$

where the summation with respect to p_1 and p_2 is performed from 0 to k_1 and k_2, respectively as seen in eq.(2.15). Here $\Xi^{r,n_1,n_2,p_1,p_2}_{k,k_1,k_2}(\chi)$ is the characteristic integral defined as

$$\begin{aligned}\Xi^{r,n_1,n_2,p_1,p_2}_{k,k_1,k_2}(\chi) &\equiv \Gamma(k_1+n_1+\frac{3}{2})\Gamma(k_2+n_2+\frac{3}{2})\left(\frac{2\kappa T}{m}\right)^3\int\int\int \exp[-(c_1^2+c_2^2)] \\ &\times\ Y_k(\mathbf{c}'_1)Y^{(p_1)}_{k_1}(\mathbf{c}_1)Y^{(p_2)}_{k_2}(\mathbf{c}_2)S^r_{k+\frac{1}{2}}(\mathbf{c}'^2_1)S^{n_1}_{k_1+\frac{1}{2}}(\mathbf{c}_1^2)S^{n_2}_{k_2+\frac{1}{2}}(\mathbf{c}_2^2)g\mathrm{d}\epsilon\mathrm{d}\mathbf{c}_2\mathrm{d}\mathbf{c}_1.\end{aligned} \qquad \text{(B.2)}$$

Note that the integrals containing products like $Y^{(p_1)}_{k_1}(\mathbf{c}_1)Z^{(p_2)}_{k_2}(\mathbf{c}_2)$ are zero, owing to the orthogonality properties of the spherical harmonic functions, while those containing $Z^{(p_1)}_{k_1}(\mathbf{c}_1)Z^{(p_2)}_{k_2}(\mathbf{c}_2)$ are identical with the corresponding integrals $\Xi^{r,n_1,n_2,p_1,p_2}_{k,k_1,k_2}(\chi)$. The factor $W^{n_1,n_2,p_1,p_2}_{k,k_1,k_2}$ in eq.(B.1) is defined as

$$\begin{aligned}W^{n_1,n_2,p_1,p_2}_{k,k_1,k_2} \equiv n^2\left(\frac{m}{2\pi\kappa T}\right)^3\left(\frac{m}{2\kappa T}\right)^{\frac{k+k_1+k_2}{2}} & n_1!n_2!(k+\frac{1}{2})\sqrt{\pi} \\ & \Psi^{p_1,p_2}_{k_1,k_2}(B^{(p_1)}_{k_1n_1}B^{(p_2)}_{k_2n_2}+C^{(p_1)}_{k_1n_1}C^{(p_2)}_{k_2n_2}),\end{aligned} \qquad \text{(B.3)}$$

which is obtained from the prefactors and the coefficients in the general form of f_1, f_2 in eq.(2.13) and Q'_{kr} in eq.(2.21). Note that $C^{(p_1)}_{k_1 n_1} C^{(p_2)}_{k_2 n_2}$ appear from the integrals containing $Z^{(p_1)}_{k_1}(\mathbf{c}_1) Z^{(p_2)}_{k_2}(\mathbf{c}_2)$, and that $B^{(0)}_{kr} = B_{kr}$ and $C^{(0)}_{kr} = 0$ from eqs.(2.15), (2.16), (2.17) and (2.18). The constant $\Psi^{p_1,p_2}_{k_1,k_2}$ is defined as

$$\Psi^{p_1,p_2}_{k_1,k_2} = 1 \quad \text{for} \quad \mathrm{p_1 = p_2 = 0}, \tag{B.4}$$

and

$$\Psi^{p_1,p_2}_{k_1,k_2} = \frac{4(k_1 - p_1)!(k_2 - p_1)!}{(k_1 + p_1)!(k_2 + p_1)!} \quad \text{for} \quad \mathrm{p_1 = p_2 \neq 0}. \tag{B.5}$$

Here $\Psi^{p_1,p_2}_{k_1,k_2}$ for $p_1 \neq p_2$ is not necessary for our calculation.[25] It is found that we need only to evaluate the characteristic integral $\Xi^{r,n_1,n_2,p_1,p_1}_{k,k_1,k_2}(\chi)$ in order to calculate $F^1_{kr}(\chi)$. Our calculation of $\Xi^{r,n_1,n_2,p_1,p_1}_{k,k_1,k_2}(\chi)$ is written in Appendix C. Our calculation has been performed mainly based on Burnett's method[25]. We have, however, made some modifications on his method, which make the calculation of $\Xi^{r,n_1,n_2,p_1,p_1}_{k,k_1,k_2}(\chi)$ much easier. (see Appendix C) We emphasize that our calculation could not be carried out completely if we did not make the modifications on Burnett's method.

Once the characteristic integral $\Xi^{r,n_1,n_2,p_1,p_1}_{k,k_1,k_2}(\chi)$ has been derived, $F^1_{kr}(\chi)$ is now calculated from eq.(B.1) with $W^{n_1,n_2,p_1,p_1}_{k,k_1,k_2}$ in eq.(B.3). Note that the coefficient term $B^{(p_1)}_{k_1 n_1} B^{(p_2)}_{k_2 n_2} + C^{(p_1)}_{k_1 n_1} C^{(p_2)}_{k_2 n_2}$ in $W^{n_1,n_2,p_1,p_1}_{k,k_1,k_2}$ can be determined for each order when the suffices k_1, k_2, n_1, n_2, p_1 and p_2 are specified.

Appendix C

Calculation of $\Xi^{r,n_1,n_2,p_1,p_2}_{k,k_1,k_2}(\chi)$

In this appendix, we explain how to calculate $\Xi^{r,n_1,n_2,p_1,p_2}_{k,k_1,k_2}(\chi)$ which appears in eq.(B.2). As is mentioned in Appendix B, we need only to evaluate the characteristic integral $\Xi^{r,n_1,n_2,p_1,p_1}_{k,k_1,k_2}(\chi)$ in order to calculate $F^1_{kr}(\chi)$: $M^{r,n_1,0,0,0}_{1,1,0}$ can be calculated from eq.(D.3) with $\Xi^{r,n_1,0,0,0}_{1,1,0}(\chi)$, $M^{r,n_1,0,0,0}_{k,k-2q,0}$ can be calculated from eq.(E.9) with $\Xi^{r,n_1,0,0,0}_{k,k-2q,0}(\chi)$, $M^{r,n_1,n_2,0,0}_{k,1,1}$ can be calculated from eq.(E.10) with $\Xi^{r,n_1,n_2,0,0}_{k,1,1}(\chi)$ and $M^{r,n_1,n_2,1,1}_{k,1,1}$ can be calculated from eq.(E.11) with $\Xi^{r,n_1,n_2,1,1}_{k,1,1}(\chi)$.

C.1 Introduction of $\Theta^{p_1,p_2}_{k,k_1,k_2}$

The relative speed g can be represented as

$$g = \frac{\Gamma(\frac{3}{2})}{\left(\frac{m}{2\kappa T}\right)^{\frac{1}{2}}} \frac{i}{2\pi} \int_{\infty}^{0+} \frac{d\Lambda}{(-\Lambda)^{\frac{3}{2}}} \exp(-\frac{m\Lambda g^2}{2\kappa T}). \tag{C.1}$$

Equation (C.1) is known as Hankel's contour integral.[25, 155] Therefore, using eq.(2.14), the characteristic integral $\Xi^{r,n_1,n_2,p_1,p_2}_{k,k_1,k_2}(\chi)$ corresponds to the coefficient of $s^{n_1}t^{n_2}u^r$ in

$$\begin{aligned}\Theta^{p_1,p_2}_{k,k_1,k_2} &\equiv \nu_{k_1,k_2,k} \frac{\Gamma(\frac{3}{2})}{\left(\frac{m}{2\kappa T}\right)^{\frac{7}{2}}} \frac{i}{2\pi} \int_{\infty}^{0+} \frac{d\Lambda}{(-\Lambda)^{\frac{3}{2}}} \int\int\int Y_k(\mathbf{c}_1') Y^{(p_1)}_{k_1}(\mathbf{c}_1) Y^{(p_2)}_{k_2}(\mathbf{c}_2) \\ &\times \exp\{-(\alpha c_1^2 + \beta c_2^2 + \gamma c_1'^2 + \frac{m\Lambda g^2}{2\kappa T})\} d\epsilon d\mathbf{c}_2 d\mathbf{c}_1, \end{aligned} \tag{C.2}$$

that is,

$$\Theta^{p_1,p_2}_{k,k_1,k_2} \equiv \sum_{r,n_1,n_2} \Xi^{r,n_1,n_2,p_1,p_2}_{k,k_1,k_2}(\chi) s^{n_1} t^{n_2} u^r. \tag{C.3}$$

In eq.(C.2) α, β and γ are defined as

$$\alpha \equiv \frac{1}{1-s}, \quad \beta \equiv \frac{1}{1-t}, \quad \gamma \equiv \frac{u}{1-u}, \tag{C.4}$$

and $\nu_{k_1,k_2,k}$ is given by

$$\nu_{k_1,k_2,k} \equiv \frac{(1-s)^{-k_1-\frac{3}{2}}(1-t)^{-k_2-\frac{3}{2}}(1-u)^{-k-\frac{3}{2}}}{\Gamma(k+r+\frac{3}{2})}. \tag{C.5}$$

It should be noted that the integration in eq.(C.1) does not appear for Maxwell molecules. This is why calculation of the velocity distribution function for Maxwell molecules becomes much easier than that for hard-core molecules. [25, 26] Finally, we need only to evaluate the characteristic integral $\Theta^{p_1,p_2}_{k,k_1,k_2}$ in order to calculate $\Xi^{r,n_1,n_2,p_1,p_2}_{k,k_1,k_2}(\chi)$.

C.2 Derivation of the Inductive Equation

In order to evaluate $\Theta^{p_1,p_2}_{k,k_1,k_2}$ in eq.(C.2), let us derive an inductive equation for $\tilde{\Theta}^{p_1,p_2}_{k,k_1,k_2}$, which is related to $\Theta^{p_1,p_2}_{k,k_1,k_2}$ by

$$\tilde{\Theta}^{p_1,p_2}_{k,k_1,k_2} \equiv \nu^{-1}_{k_1,k_2,k} \Theta^{p_1,p_2}_{k,k_1,k_2}. \tag{C.6}$$

By replacing c_{1z} and c_{2z} by $c_{1z}-w$ and $c_{2z}-w$, respectively, c'_{1z} and c'_{2z} will be changed to $c'_{1z}-w$ and $c'_{2z}-w$. At the same time, the relative speed g is not modified, and the value of $\Theta^{p_1,p_2}_{k,k_1,k_2}$ is unchanged. Therefore, $\Theta^{p_1,p_2}_{k,k_1,k_2}$ is independent of w and differentiation of $\Theta^{p_1,p_2}_{k,k_1,k_2}$ with respect to w gives zero. After this differentiation has been performed and w has been set to zero, it is found that

$$\nu_{k_1,k_2,k} \frac{\Gamma(\frac{3}{2})}{\left(\frac{m}{2\kappa T}\right)^{\frac{7}{2}}} \frac{i}{2\pi} \int_\infty^{0+} \frac{d\Lambda}{(-\Lambda)^{\frac{3}{2}}} \int\int\int \exp\{-(\alpha c_1^2 + \beta c_2^2 + \gamma c_1'^2 + \frac{m\Lambda g^2}{2\kappa T})\} d\epsilon d\mathbf{c}_2 d\mathbf{c}_1 \times$$

$$\left\{\left(\frac{2m}{\kappa T}\right)^{\frac{1}{2}}(\alpha c_{1z}+\beta c_{2z}+\gamma c'_{1z})Y_kY_{k_1}^{(p_1)}Y_{k_2}^{(p_2)}-kY_{k-1}Y_{k_1}^{(p_1)}Y_{k_2}^{(p_2)}\right.$$
$$\left.-(k_1+p_1)Y_kY_{k_1-1}^{(p_1)}Y_{k_2}^{(p_2)}-(k_2+p_2)Y_kY_{k_1}^{(p_1)}Y_{k_2-1}^{(p_2)}\right\}=0, \tag{C.7}$$

employing the formulae[25, 155]:

$$\left(\frac{m}{2\kappa T}\right)^{\frac{1}{2}}\partial_{c'_{1z}}Y_k(\mathbf{c}'_1)=kY_{k-1}(\mathbf{c}'_1),\quad \left(\frac{m}{2\kappa T}\right)^{\frac{1}{2}}\partial_{c_{iz}}Y_{k_i}^{(p_i)}(\mathbf{c}_i)=(k_i+p_i)Y_{k_i-1}^{(p_i)}(\mathbf{c}_i), \tag{C.8}$$

for i = 1 and 2. Then, by using the formulae[25, 155]

$$\left(\frac{2\kappa T}{m}\right)^{\frac{1}{2}}(2k+1)c'_{1z}Y_k(\mathbf{c}'_1)=(k+1)Y_{k+1}(\mathbf{c}'_1)+\frac{2\kappa T}{m}kc_1'^2Y_{k-1}(\mathbf{c}'_1), \tag{C.9}$$

and

$$\left(\frac{2\kappa T}{m}\right)^{\frac{1}{2}}(2k_i+1)c_{iz}Y_{k_i}^{(p_i)}(\mathbf{c}_i)=(k_i-p_i+1)Y_{k_i+1}^{(p_i)}(\mathbf{c}_i)+\frac{2\kappa T}{m}(k_i+p_i)c_i^2Y_{k_i-1}^{(p_i)}(\mathbf{c}_i), \tag{C.10}$$

for i = 1 and 2, eq.(C.7) becomes

$$\frac{\Gamma(\frac{3}{2})}{\left(\frac{m}{2\kappa T}\right)^{\frac{7}{2}}}\frac{i}{2\pi}\int_\infty^{0+}\frac{d\Lambda}{(-\Lambda)^{\frac{3}{2}}}\int\int\int\exp\{-(\alpha c_1^2+\beta c_2^2+\gamma c_1'^2+\frac{m\Lambda g^2}{2\kappa T})\}d\epsilon d\mathbf{c}_2d\mathbf{c}_1\times$$
$$\left\{Y_kY_{k_2}^{(p_2)}[\frac{m\alpha}{\kappa T(2k_1+1)}\{(k_1-p_1+1)Y_{k_1+1}^{(p_1)}+\frac{2\kappa T}{m}(k_1+p_1)Y_{k_1-1}^{(p_1)}c_1^2\}-(k_1+p_1)Y_{k_1-1}^{(p_1)}]\right.$$
$$+Y_kY_{k_1}^{(p_1)}[\frac{m\beta}{\kappa T(2k_2+1)}\{(k_2-p_2+1)Y_{k_2+1}^{(p_2)}+\frac{2\kappa T}{m}(k_2+p_2)Y_{k_2-1}^{(p_2)}c_2^2\}-(k_2+p_2)Y_{k_2-1}^{(p_2)}]$$
$$\left.+Y_{k_1}^{(p_1)}Y_{k_2}^{(p_2)}[\frac{m\gamma}{\kappa T(2k+1)}\{(k+1)Y_{k+1}+\frac{2\kappa T}{m}kY_{k-1}c_1'^2\}-kY_{k-1}]\right\}=0. \tag{C.11}$$

From eqs.(C.2) and (C.6), eq.(C.11) leads to the inductive equation

$$\frac{m\alpha(k_1-p_1+1)}{\kappa T(2k_1+1)}\tilde{\Theta}_{k,k_1+1,k_2}^{p_1,p_2}-\frac{2\alpha(k_1+p_1)}{(2k_1+1)}\frac{\partial\tilde{\Theta}_{k,k_1-1,k_2}^{p_1,p_2}}{\partial\alpha}-(k_1+p_1)\tilde{\Theta}_{k,k_1-1,k_2}^{p_1,p_2}$$

$$+\frac{m\beta(k_2-p_2+1)}{\kappa T(2k_2+1)}\tilde{\Theta}^{p_1,p_2}_{k,k_1,k_2+1}-\frac{2\beta(k_2+p_2)}{(2k_2+1)}\frac{\partial\tilde{\Theta}^{p_1,p_2}_{k,k_1,k_2-1}}{\partial\beta}-(k_2+p_2)\tilde{\Theta}^{p_1,p_2}_{k,k_1,k_2-1}$$
$$+\frac{m\gamma(k+1)}{\kappa T(2k+1)}\tilde{\Theta}^{p_1,p_2}_{k+1,k_1,k_2}-\frac{2\gamma k}{(2k+1)}\frac{\partial\tilde{\Theta}^{p_1,p_2}_{k-1,k_1,k_2}}{\partial\gamma}-k\tilde{\Theta}^{p_1,p_2}_{k-1,k_1,k_2}=0, \tag{C.12}$$

for $\tilde{\Theta}^{p_1,p_2}_{k,k_1,k_2}$. Because of this inductive equation, once the initial value $\tilde{\Theta}^{p_1,p_2}_{0,k_1,k_2}$ is known for all k_1, k_2, p_1 and p_2, then the values of the integral $\tilde{\Theta}^{p_1,p_2}_{k,k_1,k_2}$ for any k, k_1, k_2, p_1 and p_2, can be obtained, and $\Theta^{p_1,p_2}_{k,k_1,k_2}$ is then obtained from eq.(C.6).

Burnett[25] chose to work with $\tilde{\Theta}^{p_1,p_2}_{k,k_1,k_2}(\Lambda)$ (*i.e.* before integration by Λ) rather than $\tilde{\Theta}^{p_1,p_2}_{k,k_1,k_2}$, and he derived an inductive equation for that quantity; he then calculated $\tilde{\Theta}^{p_1,p_2}_{k,k_1,k_2}$ by integrating his result over Λ. We, however, have chosen to work with $\tilde{\Theta}^{p_1,p_2}_{k,k_1,k_2}$ in our calculation. As a result, the calculation of $\Theta^{p_1,p_2}_{k,k_1,k_2}$ becomes much easier.

C.3 Calculation of the Initial Value

The initial value of the inductive equation (C.12), *i.e.* $\tilde{\Theta}^{p_1,p_2}_{0,k_1,k_2}$, has been calculated and written explicitly in ref.[25], so that we do not carry out the derivation of the initial value here. We note that, although Burnett chose the value of $\tilde{\Theta}^{p_1,p_2}_{0,k_1,k_2}(\Lambda)$ as the appropriate initial value, he also calculated $\tilde{\Theta}^{p_1,p_2}_{0,k_1,k_2}$. The result is that the initial value $\tilde{\Theta}^{p_1,p_2}_{0,k_1,k_2}$ is zero unless $k_1=k_2$ and $p_1=p_2$, in which case it is the coefficient of y^{k_1} in

$$\Upsilon^{p_1}_{k_1} \equiv \iota^{p_1}_{k_1}(\alpha+\beta+\gamma-y)^{\frac{1}{2}}\int_0^\pi \frac{d\xi}{\{\alpha\beta+\alpha\gamma\sin^2\frac{\chi}{2}+\beta\gamma\cos^2\frac{\chi}{2}-\frac{1}{2}i\gamma y\sin\chi\cos\xi\}^2}, \tag{C.13}$$

that is,

$$\Upsilon^{p_1}_{k_1}=\iota^{p_1}_{k_1}\sum_{k_1}\frac{\tilde{\Theta}^{p_1,p_1}_{0,k_1,k_1}}{\iota^{p_1}_{k_1}}y^{k_1}, \tag{C.14}$$

where the prefactor $\iota_{k_1}^{p_1}$ is given by

$$\iota_{k_1}^{p_1} \equiv \eta \frac{(k_1+p_1)!}{(k_1-p_1)!} \frac{k_1!}{k_1+\frac{1}{2}} \frac{\pi^{\frac{5}{2}}}{\left(\frac{m}{2\kappa T}\right)^{k_1+\frac{7}{2}}}, \tag{C.15}$$

with $\eta = 1+\delta_{0,p_1}$. It is convenient to expand the integrand in powers of $\cos\xi$ before carrying out the integration with respect to ξ in eq.(C.13). [25] Note that $\Theta_{0,k_1,k_2}^{p_1,p_2}$ is obtained by $\nu_{k_1,k_2,0}\tilde{\Theta}_{0,k_1,k_2}^{p_1,p_2}$ from eq.(C.6).

C.4 Evaluation of $\Xi_{k,k_1,k_2}^{r,n_1,n_2,p_1,p_1}(\chi)$

Using the inductive equation (C.12) and the initial value $\tilde{\Theta}_{0,k_1,k_1}^{p_1,p_1}$ calculated in section C.3, the values of the integral $\Theta_{k,k_1,k_2}^{p_1,p_2}$ for any k, k_1, k_2, p_1 and p_2, can be obtained with the relation (C.6). The result is that $\Theta_{k,k_1,k_2}^{p_1,p_2}$ vanishes unless $p_1 = p_2$ and $k = |k_1 - k_2| + 2q$, where q is a positive integer or zero. In order to obtain $\Xi_{k,k_1,k_2}^{r,n_1,n_2,p_1,p_1}(\chi)$, it is sufficient to have $\Theta_{k,k_1,k_2}^{p_1,p_1}$ only for $k_1 \geq k_2$. This is because the value of $\Xi_{k,k_1,k_2}^{r,n_1,n_2,p_1,p_1}(\chi)$, with k_1 and k_2, n_1 and n_2 interchanged, corresponds to the value of $\Xi_{k,k_1,k_2}^{r,n_1,n_2,p_1,p_1}(\chi)$ with χ replaced by $\pi - \chi$. Thus, if $k_1 \neq k_2$ or $n_1 \neq n_2$, $\Xi_{k,k_1,k_2}^{r,n_1,n_2,p_1,p_1}(\chi)$ for any set of k_1 and k_2, n_1 and n_2 corresponds to

$$\Xi_{k,k_1,k_2}^{r,n_1,n_2,p_1,p_1}(\chi) = \Xi_{k,k_1,k_2}^{r,n_1,n_2,p_1,p_1}(\chi) + \Xi_{k,k_1,k_2}^{r,n_1,n_2,p_1,p_1}(\pi-\chi), \tag{C.16}$$

for $k_1 \geq k_2$; if $k_1 = k_2$ and $n_1 = n_2$, then $\Xi_{k,k_1,k_2}^{r,n_1,n_2,p_1,p_1}(\chi)$ gives the required value at once.[25]

Appendix D

Calculation of the First Order Coefficients $B^{\rm I}_{kr}$

Let us explain how to obtain the first-order coefficients, that is, how to solve the integral equation (2.4). To begin with, we calculate $\Omega^{\rm H}_{kr}$ in eq.(2.25) to first order; $\Omega^{\rm H}_{kr}$ for first order corresponds to the right-hand side of eq.(2.4). For first order, $\Omega^{\rm H}_{kr}$ in eq.(2.25) can be calculated by substituting $B_{00}=1$ into the expressions of $D_{k,r}$, $E_{k,r}$ and $G_{k,r}$ in eqs.(A.7), (A.8) and (A.9): the coefficient $B_{00}=1$ corresponds to $f_1=f_1^{(0)}$, and higher-order terms do not appear in $\Omega^{\rm H}_{kr}$ for first order. $\Omega^{\rm H}_{kr}$ for first order finally becomes

$$\Omega^{\rm H}_{1r}=-\frac{n}{T}\left(\frac{m}{2\kappa T}\right)^{-\frac{1}{2}}\frac{\partial T}{\partial z}\delta_{1,r}. \tag{D.1}$$

Now $\Omega^{\rm H}_{kr}$ for first order is found to vanish unless $k=1$, so that we need calculate only $\Delta^{\rm H}_{1,r}$ for first order; as was mentioned in the end of §2.1, we do not need to consider the case in which the right-hand side of eq.(2.4) becomes zero.[3] To derive $\Delta^{\rm H}_{1,r}$ in eq.(2.27) for first order, we must calculate both $W^{n_1,n_2,p_1,p_1}_{1,k_1,k_2}$ and $\Xi^{r,n_1,n_2,p_1,p_1}_{1,k_1,k_2}$ in $F^1_{1,r}(\chi)$ of eq.(B.1) for first order as was shown in the previous subsection. The result for $\Delta^{\rm H}_{1,r}$ to first order can be written finally in the form

$$\Delta^{\rm H}_{1r}=B_{00}\sum_{n_1}B^{\rm I}_{1n_1}M^{r,n_1,0,0,0}_{1,1,0}, \tag{D.2}$$

where the set of the coefficients $B^{\rm I}_{1n_1}B_{00}$ is obtained from $W^{n_1,0,0,0}_{1,1,0}$ in eq.(B.3). f_1 in eq.(2.28) contains only $B_{00}=1$ and the first-order coefficients, i.e. the

family of $B^{\rm I}_{k_1 n_1}$ to first order; f_2 in eq.(2.28) also contains $B_{00}=1$ and the family of $B^{\rm I}_{k_2 n_2}$ to first order. Thus, we obtain only the term $B^{\rm I}_{1n_1}B_{00}$ from $W^{n_1,0,0,0}_{1,1,0}$ to first order using the fact that $F^1_{kr}(\chi)=0$ unless $k=|k_1-k_2|+2q$. Note that it is sufficient to consider only the case for $k_1 \geq k_2$ as is explained in ref.[25] and Appendix C, and that we set $q=0$. The matrix $M^{r,n_1,0,0,0}_{1,1,0}$ is thus obtained

$$\begin{aligned} M^{r,n_1,0,0,0}_{1,1,0} &= \frac{3n^2\sigma^2m^4n_1!}{64\pi^{\frac{5}{2}}\kappa^4T^4} \\ &\times \int_0^\pi [\Xi^{r,n_1,0,0,0}_{1,1,0}(\chi)-\Xi^{r,n_1,0,0,0}_{1,1,0}(0)]\sin\frac{\chi}{2}\cos\frac{\chi}{2}{\rm d}\chi, \end{aligned} \tag{D.3}$$

using eqs.(2.27), (B.1) and (B.3).

For $k=1$, eq.(2.31) gives simultaneous equations determining the first-order coefficients $B^{\rm I}_{1n_1}$, i.e.

$$\Omega^{\rm H}_{1r}=\sum_{n_1\geq 1}B^{\rm I}_{1n_1}M^{r,n_1,0,0,0}_{1,1,0}, \tag{D.4}$$

from eqs.(D.1) and (D.2). Note that we need only to obtain the first-order coefficients $B^{\rm I}_{1n_1}$ for $n_1 \geq 1$, because $B_{10}=0$ from eq.(2.19). We have calculated the matrix $M^{r,n_1,0,0,0}_{1,1,0}$ for $1\leq r\leq 7$ and $1\leq n_1\leq 7$ from eq.(D.3), and we have confirmed that $M^{0,n_1,0,0,0}_{1,1,0}$ for $1\leq n_1\leq 7$ calculated from eq.(D.3) vanishes. Our result for $M^{r,n_1,0,0,0}_{1,1,0}$ for $1\leq r\leq 7$ and $1\leq n_1\leq 7$ is given in Appendix F. At last, we can determine the first-order coefficients $B^{\rm I}_{1n_1}$ by solving the simultaneous equations (D.4), that is, $B^{\rm I}_{1n_1}$ can be obtained as

$$B^{\rm I}_{1n_1}=\sum_{r\geq 1}\Omega^{\rm H}_{1r}(M^{r,n_1,0,0,0}_{1,1,0})^{-1}, \tag{D.5}$$

where X^{-1} represents the inverse matrix of a matrix X. Note that we have confirmed, using eqs.(D.1) and (D.3), that both sides of eq.(D.4) for $r=0$ vanish, so that we need only calculate both sides of eq.(D.4) for $r\geq 1$. Finally, the results of the first-order coefficients $B^{\rm I}_{k_1n_1}$, i.e. $B^{\rm I}_{kr}$ in eq.(2.15) can be calculated as in eq.(2.32).

Appendix E

Calculation of the Second Order Coefficients $B_{kr}^{\rm II}$

Let us explain how to obtain the second-order coefficients, that is, how to solve the integral equation (2.5). The coefficients of first order, i.e. the family of $B_{kr}^{\rm I}$, have been obtained as given in eq.(2.32), so that we can employ them to determine the second-order coefficients, i.e. the family of $B_{kr}^{\rm II}$.

To begin with, we calculate $\Omega_{kr}^{\rm H}$ in eq.(2.25) for second order; $\Omega_{kr}^{\rm H}$ for second order corresponds to the first term on the right-hand side of eq.(2.5). For second order, $\Omega_{kr}^{\rm H}$ in eq.(2.25) can be calculated by substituting the family of $B_{kr}^{\rm I}$ into the expressions of $D_{k,r}$, $E_{k,r}$ and $G_{k,r}$ in eqs.(A.7), (A.8) and (A.9); other terms do not appear in $\Omega_{kr}^{\rm H}$ for second order. The results of the tedious calculation of $\Omega_{kr}^{\rm H}$ to second order finally become as follows. For $k=0$, $\Omega_{0r}^{\rm H}$ becomes

$$\Omega_{0r}^{\rm H} = 0, \tag{E.1}$$

for $r=0$ and 1,

$$\Omega_{02}^{\rm H} = \frac{35}{32}\frac{1}{\sqrt{2\pi}\sigma^2 T^2}\left(\frac{m}{2\kappa T}\right)^{-\frac{1}{2}}\left\{(\nabla T)^2\left(\frac{21}{4}b_{12}-4b_{11}\right)+T(\nabla^2 T)\left(\frac{7}{2}b_{12}-b_{11}\right)\right\}, \tag{E.2}$$

for $r=2$, and

$$\Omega_{0r}^{\rm H} = \frac{5}{16}\frac{1}{\sqrt{2\pi}\sigma^2 T^2}\left(\frac{m}{2\kappa T}\right)^{-\frac{1}{2}}\left\{T(\nabla^2 T)\left[(r+\frac{3}{2})b_{1r}-b_{1,r-1}\right]\right.$$

$$+ \quad (\nabla T)^2 \left[(r^2 + r - \frac{3}{4}) b_{1r} - 2r b_{1,r-1} + b_{1,r-2} \right] \Big\}, \tag{E.3}$$

for $r \geq 3$. Note that values for the constants b_{1r} are summarized in Table 2.1. For $k = 2$, $\Omega^{\rm H}_{2r}$ becomes

$$\begin{aligned} \Omega^{\rm H}_{20} &= \frac{5}{16} \frac{1}{\sqrt{2\pi}\sigma^2 T^2} \left(\frac{m}{2\kappa T} \right)^{-\frac{1}{2}} \left\{ -\frac{b_{11}}{2} \left[2 \left(\partial_z T \right)^2 - \left(\partial_x T \right)^2 - \left(\partial_y T \right)^2 \right] \right. \\ &- \left. b_{11} T \left[2\partial_z^2 T - \partial_x^2 T - \partial_y^2 T \right] \right\}, \end{aligned} \tag{E.4}$$

and

$$\begin{aligned} \Omega^{\rm H}_{21} &= \frac{5}{16} \frac{1}{\sqrt{2\pi}\sigma^2 T^2} \left(\frac{m}{2\kappa T} \right)^{-\frac{1}{2}} \left\{ \left[2 \left(\partial_z T \right)^2 - \left(\partial_x T \right)^2 - \left(\partial_y T \right)^2 \right] \left[\frac{5}{2} b_{11} - 3 b_{12} \right] \right. \\ &+ \left. T \left[2\partial_z^2 T - \partial_x^2 T - \partial_y^2 T \right] \left[b_{11} - 2 b_{12} \right] \right\}, \end{aligned} \tag{E.5}$$

and

$$\begin{aligned} \Omega^{\rm H}_{2r} &= \frac{5}{16} \frac{1}{\sqrt{2\pi}\sigma^2 T^2} \left(\frac{m}{2\kappa T} \right)^{-\frac{1}{2}} \\ &\times \left\{ \left[2 \left(\partial_z T \right)^2 - \left(\partial_x T \right)^2 - \left(\partial_y T \right)^2 \right] \left[-(r+1)(r+\frac{1}{2}) b_{1,r+1} + (2r + \frac{1}{2}) b_{1r} - b_{1,r-1} \right] \right. \\ &+ \left. T \left[2\partial_z^2 T - \partial_x^2 T - \partial_y^2 T \right] \left[-(r+1) b_{1,r+1} + b_{1r} \right] \right\}, \end{aligned} \tag{E.6}$$

for $r \geq 2$. For $k = 1$ and $k \geq 3$, we find that $\Omega^{\rm H}_{kr}$ becomes

$$\Omega^{\rm H}_{kr} = 0, \tag{E.7}$$

for any value of r.

Next let us calculate $\Delta^{\rm H}_{kr}$ in eq.(2.27) for second order. In order to derive $\Delta^{\rm H}_{kr}$ for second order, we have to calculate $W^{n_1,n_2,p_1,p_1}_{k,k_1,k_2}$ and $\Xi^{r,n_1,n_2,p_1,p_1}_{k,k_1,k_2}$ in $F^1_{kr}(\chi)$ of eq.(B.1) to second order, as was shown in Appendix B. For even k, $\Delta^{\rm H}_{kr}$ to second order results in the general form:

$$\begin{aligned} \Delta^{\rm H}_{kr} &= B_{00} \sum_{n_1, 0 \leq q \leq \frac{k}{2}} B^{\rm II}_{k-2q,n_1} M^{r,n_1,0,0,0}_{k,k-2q,0} + \sum_{n_1,n_2} B^{\rm I}_{1n_1} B^{\rm I}_{1n_2} M^{r,n_1,n_2,0,0}_{k,1,1} \\ &+ \sum_{n_1,n_2} [B^{(1){\rm I}}_{1n_1} B^{(1){\rm I}}_{1n_2} + C^{(1){\rm I}}_{1n_1} C^{(1){\rm I}}_{1n_2}] M^{r,n_1,n_2,1,1}_{k,1,1}. \end{aligned} \tag{E.8}$$

Here the set of the coefficients $B^{\rm II}_{k-2q,n_1}B_{00}$ can be obtained from $W^{n_1,0,0,0}_{k,k-2q,0}$ in eq.(B.3). The set of the coefficients $B^{\rm I}_{1n_1}B^{\rm I}_{1n_2}$ is obtained from $W^{n_1,n_2,0,0}_{k,1,1}$ in eq.(B.3); $B^{\rm I}_{1n_1}$ from f_1 and $B^{\rm I}_{1n_2}$ from f_2 are the first-order coefficients obtained in eq.(2.32), so that $B^{\rm I}_{1n_1}B^{\rm I}_{1n_2}$ is second order. Similarly, the set of the terms $B^{(1){\rm I}}_{1n_1}B^{(1){\rm I}}_{1n_2}+C^{(1){\rm I}}_{1n_1}C^{(1){\rm I}}_{1n_2}$ is obtained from $W^{n_1,n_2,1,1}_{k,1,1}$ in eq.(B.3); $B^{(1){\rm I}}_{1n_1}$, $C^{(1){\rm I}}_{1n_1}$ from f_1 and $B^{(1){\rm I}}_{1n_2}$, $C^{(1){\rm I}}_{1n_2}$ from f_2 are the first-order coefficients obtained in 2.2.3, so that $B^{(1){\rm I}}_{1n_1}B^{(1){\rm I}}_{1n_2}$ and $C^{(1){\rm I}}_{1n_1}C^{(1){\rm I}}_{1n_2}$ are also second order. To second order, f_1 of eq.(2.28) contains only $B_{00}=1$, the family of $B^{\rm I}_{k_1n_1}$ obtained as eq.(2.32) and the family of $B^{\rm II}_{k_1n_1}$ to be determined here; f_2 of eq.(2.28) also contains only $B_{00}=1$, the family of $B^{\rm I}_{k_2n_2}$ and the family of $B^{\rm II}_{k_2n_2}$ to second order. Thus, we can only obtain the sets of the terms in eq.(E.8) for second order by using the fact that $F^1_{kr}(\chi)=0$ unless $k=|k_1-k_2|+2q$: the second and the third terms on the right-hand side of eq.(E.8) do not appear for odd k. Note that it is sufficient to consider only the case for $k_1\geq k_2$, as is explained in ref.[25] and Appendix C, and that $B^{(1){\rm I}}_{1n_1}C^{(1){\rm I}}_{1n_2}$ or $C^{(1){\rm I}}_{1n_1}B^{(1){\rm I}}_{1n_2}$ does not appear owing to the orthogonality properties of the spherical harmonic functions. (see Appendix B) The matrix $M^{r,n_1,0,0,0}_{k,k-2q,0}$ in eq.(E.8) is thus obtained as

$$\begin{aligned} M^{r,n_1,0,0,0}_{k,k-2q,0} &= \frac{n^2\sigma^2}{2}\left(\frac{m}{2\pi\kappa T}\right)^3\left(\frac{m}{2\kappa T}\right)^{k-q} n_1!(k+\frac{1}{2})\sqrt{\pi} \\ &\times \int_0^\pi [\Xi^{r,n_1,0,0,0}_{k,k-2q,0}(\chi)-\Xi^{r,n_1,0,0,0}_{k,k-2q,0}(0)]\sin\frac{\chi}{2}\cos\frac{\chi}{2}{\rm d}\chi, \end{aligned} \tag{E.9}$$

using eqs.(2.27), (B.1) and (B.3). Similarly, the matrices $M^{r,n_1,n_2,0,0}_{k,1,1}$ and $M^{r,n_1,n_2,1,1}_{k,1,1}$ in eq.(E.8) are derived as

$$\begin{aligned} M^{r,n_1,n_2,0,0}_{k,1,1} &= \frac{n^2\sigma^2}{2}\left(\frac{m}{2\pi\kappa T}\right)^3\left(\frac{m}{2\kappa T}\right)^{\frac{k}{2}+1} n_1!n_2!(k+\frac{1}{2})\sqrt{\pi} \\ &\times \int_0^\pi [\Xi^{r,n_1,n_2,0,0}_{k,1,1}(\chi)-\Xi^{r,n_1,n_2,0,0}_{k,1,1}(0)]\sin\frac{\chi}{2}\cos\frac{\chi}{2}{\rm d}\chi, \end{aligned} \tag{E.10}$$

and

$$\begin{aligned} M^{r,n_1,n_2,1,1}_{k,1,1} &= \frac{n^2\sigma^2}{2}\left(\frac{m}{2\pi\kappa T}\right)^3\left(\frac{m}{2\kappa T}\right)^{\frac{k}{2}+1} n_1!n_2!(k+\frac{1}{2})\sqrt{\pi} \\ &\times \int_0^\pi [\Xi^{r,n_1,n_2,1,1}_{k,1,1}(\chi)-\Xi^{r,n_1,n_2,1,1}_{k,1,1}(0)]\sin\frac{\chi}{2}\cos\frac{\chi}{2}{\rm d}\chi, \end{aligned} \tag{E.11}$$

respectively.

For even k, eq.(2.31) finally leads to simultaneous equations to determine the second-order coefficients $B^{\rm II}_{k-2q,n_1}$:

$$\begin{aligned}\Omega^{\rm H}_{kr} &= \sum_{n_1,0\le q\le \frac{k}{2}} B^{\rm II}_{k-2q,n_1} M^{r,n_1,0,0,0}_{k,k-2q,0} + \sum_{n_1,n_2} B^{\rm I}_{1n_1} B^{\rm I}_{1n_2} M^{r,n_1,n_2,0,0}_{k,1,1} \\ &+ \sum_{n_1,n_2} [B^{(1)\rm I}_{1n_1} B^{(1)\rm I}_{1n_2} + C^{(1)\rm I}_{1n_1} C^{(1)\rm I}_{1n_2}] M^{r,n_1,n_2,1,1}_{k,1,1}, \end{aligned} \tag{E.12}$$

from eq.(E.8). The second and the third terms on the right-hand side of eq.(E.12) correspond to $J(f^{(1)}_1, f^{(1)}_2)$ in the integral equation (2.5). Thus, it had been believed that eq.(E.12) should be considered for all even k because the contribution from the right-hand side of eq.(2.5) would not become zero even when $\Omega^{\rm H}_{kr}$ which corresponds to the first term on the right-hand side of eq.(2.5) is zero.[25] However, for $k = 4$, 6 and 8, we have confirmed that the second and the third terms on the right hand side of eq.(E.12) disappear, which leads to the fact that it is not necessary to consider eq.(E.12) for $k = 4$, 6 and 8. Therefore, it is natural to expect that we do not need to consider eq.(E.12) for even k furthermore. Our contention that the second and the third terms on the right hand side of eq.(E.12) will disappear for $k = 2n$ with the integer $n \ge 2$ should be demonstrated by a mathematical proof in the future. It should be mentioned that the second and the third terms on the right-hand side of eq.(E.12) do not appear for odd k, and $\Omega^{\rm H}_{kr}$ to second order is found to be zero for odd k, so that we do not need to calculate $\Delta^{\rm H}_{kr}$ for odd k; it is not necessary to consider the case in which contribution from the right-hand side of eq.(2.5) becomes zero.[3]

Now, we need to consider eq.(E.12) only for $k = 0$ and 2. If $k = 0$, eq.(E.12) leads to simultaneous equations to determine the second-order coefficients $B^{\rm II}_{0n_1}$:

$$\begin{aligned}\Omega^{\rm H}_{0r} &= \sum_{n_1\ge 2} B^{\rm II}_{0n_1} M^{r,n_1,0,0,0}_{0,0,0} + \sum_{n_1,n_2} B^{\rm I}_{1n_1} B^{\rm I}_{1n_2} M^{r,n_1,n_2,0,0}_{0,1,1} \\ &+ \sum_{n_1,n_2} [B^{(1)\rm I}_{1n_1} B^{(1)\rm I}_{1n_2} + C^{(1)\rm I}_{1n_1} C^{(1)\rm I}_{1n_2}] M^{r,n_1,n_2,1,1}_{0,1,1}, \end{aligned} \tag{E.13}$$

that is,

$$B^{\rm II}_{0n_1} = \sum_{r\ge 2} \Bigg\{ \Omega^{\rm H}_{0r} - \sum_{n_1,n_2} B^{\rm I}_{1n_1} B^{\rm I}_{1n_2} M^{r,n_1,n_2,0,0}_{0,1,1}$$

$$- \sum_{n_1,n_2} [B^{(1)\mathrm{I}}_{1n_1} B^{(1)\mathrm{I}}_{1n_2} + C^{(1)\mathrm{I}}_{1n_1} C^{(1)\mathrm{I}}_{1n_2}] M^{r,n_1,n_2,1,1}_{0,1,1} \Bigg\} (M^{r,n_1,0,0,0}_{0,0,0})^{-1}, \tag{E.14}$$

with Ω^{H}_{0r} in eqs.(E.1), (E.2) and (E.3). We should derive the second-order coefficients $B^{\mathrm{II}}_{0n_1}$ only for $n_1 \geq 2$, because $B_{00} = 1$ and $B_{01} = 0$ from eq.(2.19). We have calculated the matrix $M^{r,n_1,0,0,0}_{0,0,0}$ for $2 \leq r \leq 6$ and $2 \leq n_1 \leq 6$ from eq.(E.9), and we have confirmed that $M^{r,n_1,0,0,0}_{0,0,0}$ vanishes for $r = 0, 1$ and $2 \leq n_1 \leq 6$. We have also calculated the matrices $M^{r,n_1,n_2,0,0}_{0,1,1}$ for $2 \leq r \leq 6$, $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ from eq.(E.10), and we have confirmed $M^{r,n_1,n_2,0,0}_{0,1,1}$ vanishes for $r = 0, 1$, $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$. Our results for $M^{r,n_1,0,0,0}_{0,0,0}$ for $2 \leq r \leq 6$ and $2 \leq n_1 \leq 6$ and $M^{r,n_1,n_2,0,0}_{0,1,1}$ for $2 \leq r \leq 6$, $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ are given in Appendix F. The matrices $M^{r,n_1,n_2,1,1}_{0,1,1}$ for $2 \leq r \leq 6$, $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$, which can be calculated from eq.(E.11), are also obtained from the symmetric relation $M^{r,n_1,n_2,0,0}_{0,1,1} = M^{r,n_1,n_2,1,1}_{0,1,1}$ arising from properties of the spherical harmonic function. Finally, we can determine the second-order coefficients $B^{\mathrm{II}}_{0n_1}$ in f_1, i.e. B^{II}_{0r} in eq.(2.13) as in eq.(2.38).

If $k = 2$, eq.(E.12) leads to simultaneous equations to determine the second-order coefficients $B^{\mathrm{II}}_{2n_1}$:

$$\begin{aligned} \Omega^{\mathrm{H}}_{2r} &= \sum_{n_1 \geq 0} [B^{\mathrm{II}}_{2n_1} M^{r,n_1,0,0,0}_{2,2,0} + B^{\mathrm{II}}_{0n_1} M^{r,n_1,0,0,0}_{2,0,0}] + \sum_{n_1,n_2} B^{\mathrm{I}}_{1n_1} B^{\mathrm{I}}_{1n_2} M^{r,n_1,n_2,0,0}_{2,1,1} \\ &+ \sum_{n_1,n_2} [B^{(1)\mathrm{I}}_{1n_1} B^{(1)\mathrm{I}}_{1n_2} + C^{(1)\mathrm{I}}_{1n_1} C^{(1)\mathrm{I}}_{1n_2}] M^{r,n_1,n_2,1,1}_{2,1,1}, \end{aligned} \tag{E.15}$$

that is,

$$\begin{aligned} B^{\mathrm{II}}_{2n_1} = \sum_{r \geq 0} \Bigg\{ & \Omega^{\mathrm{H}}_{2r} - \sum_{n_1,n_2} B^{\mathrm{I}}_{1n_1} B^{\mathrm{I}}_{1n_2} M^{r,n_1,n_2,0,0}_{2,1,1} \\ & - \sum_{n_1,n_2} [B^{(1)\mathrm{I}}_{1n_1} B^{(1)\mathrm{I}}_{1n_2} + C^{(1)\mathrm{I}}_{1n_1} C^{(1)\mathrm{I}}_{1n_2}] M^{r,n_1,n_2,1,1}_{2,1,1} \Bigg\} (M^{r,n_1,0,0,0}_{2,2,0})^{-1}, \end{aligned} \tag{E.16}$$

with Ω^{H}_{2r} in eqs.(E.4), (E.5), and (E.6). Note that we have confirmed $M^{r,n_1,0,0,0}_{2,0,0}$ in eq.(E.15) becomes zero, which had been also confirmed by Burnett[25]. We should derive the second-order coefficients $B^{\mathrm{II}}_{2n_1}$ for $n_1 \geq 0$. We have calculated the matrix $M^{r,n_1,0,0,0}_{2,2,0}$ for $0 \leq r \leq 6$ and $0 \leq n_1 \leq 6$ from eq.(E.9), and also the matrices $M^{r,n_1,n_2,0,0}_{2,1,1}$ for $0 \leq r \leq 6$, $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ from eq.(E.10). Our results are given in Appendix F. The

matrices $M_{2,1,1}^{r,n_1,n_2,1,1}$ for $0 \leq r \leq 6$, $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$, which can be calculated from eq.(E.11), are also obtained from the symmetric relation $M_{2,1,1}^{r,n_1,n_2,0,0} = -2M_{2,1,1}^{r,n_1,n_2,1,1}$ arising from properties of the spherical harmonic function.[25] The second-order coefficients $B_{k_1 n_1}^{\mathrm{II}}$ in f_1, i.e. B_{kr}^{II} in eq.(2.15) can be written in the final form shown in eq.(2.39).

Appendix F

Matrix Elements

F.1 $M^{r,n_1,0,0,0}_{1,1,0}$ for $1 \leq r \leq 7$ and $1 \leq n_1 \leq 7$

The matrix elements $M^{r,n_1,0,0,0}_{1,1,0}$ for $1 \leq r \leq 7$ and $1 \leq n_1 \leq 7$ divided by $M^{1,1,0,0,0}_{1,1,0} = -\frac{16}{15}\left(\frac{m}{2\kappa T}\right)^{-\frac{1}{2}}\sqrt{2\pi}n^2\sigma^2$ calculated from eq.(D.3) are given as follows.

$$\begin{pmatrix}
1 & -5.000\times10^{-1} & -1.875\times10^{-1} & -1.875\times10^{-1} & -2.930\times10^{-1} & -6.152\times10^{-1} & -1.615 \\
-7.143\times10^{-2} & 1.607 & -1.379 & -7.902\times10^{-1} & -1.117 & -2.342 & -6.345 \\
-1.984\times10^{-3} & -1.022\times10^{-1} & 2.105 & -2.523 & -1.932 & -3.516 & -9.205 \\
-9.019\times10^{-5} & -2.661\times10^{-3} & -1.147\times10^{-1} & 2.532 & -3.883 & -3.717 & -8.264 \\
-4.336\times10^{-6} & -1.158\times10^{-4} & -2.702\times10^{-3} & -1.195\times10^{-1} & 2.911 & -5.431 & -6.237 \\
-2.023\times10^{-7} & -5.391\times10^{-6} & -1.093\times10^{-4} & -2.542\times10^{-3} & -1.207\times10^{-1} & 3.254 & -7.145 \\
-8.927\times10^{-8} & -2.455\times10^{-7} & -4.808\times10^{-6} & -9.497\times10^{-5} & -2.330\times10^{-3} & -1.201\times10^{-1} & 3.568
\end{pmatrix}$$

F.2 $M^{r,n_1,0,0,0}_{0,0,0}$ for $2 \leq r \leq 6$ and $2 \leq n_1 \leq 6$, and $M^{r,n_1,n_2,0,0}_{0,1,1}$ for $2 \leq r \leq 6$, $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$

The matrix elements $M^{r,n_1,0,0,0}_{0,0,0}$ for $2 \leq r \leq 6$ and $2 \leq n_1 \leq 6$ divided by $M^{2,2,0,0,0}_{0,0,0} = -\frac{16}{15}\left(\frac{m}{2\kappa T}\right)^{-\frac{1}{2}}\sqrt{2\pi}n^2\sigma^2$ calculated from eq.(E.9) are given as

$$\begin{pmatrix} 1 & -7.500\times10^{-1} & -3.750\times10^{-1} & -4.688\times10^{-1} & -8.789\times10^{-1} \\ -7.143\times10^{-2} & 1.661 & -1.795 & -1.239 & -2.047 \\ -1.984\times10^{-3} & -9.970\times10^{-2} & 2.179 & -3.068 & -2.699 \\ -9.019\times10^{-5} & -2.503\times10^{-3} & -1.116\times10^{-1} & 2.616 & -4.537 \\ -4.336\times10^{-6} & -1.060\times10^{-4} & -2.517\times10^{-3} & -1.163\times10^{-1} & 2.998 \end{pmatrix}$$

The matrix elements $M^{2,n_1,n_2,0,0}_{0,1,1}$ for $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ divided by $M^{2,1,1,0,0}_{0,1,1} = -\frac{2}{45}\left(\frac{m}{2\kappa T}\right)^{-\frac{1}{2}}\sqrt{2\pi}n^2\sigma^2$ calculated from eq.(E.10) are given as

$$\begin{pmatrix} 1 & 0.500 & 0.000 & -9.375\times10^{-1} & -4.102 & -1.661\times10^{1} & -7.106\times10^{1} \\ 0.500 & 3.750\times10^{-1} & 9.375\times10^{-1} & 8.203\times10^{-1} & -1.846 & -2.030\times10^{1} & -1.320\times10^{2} \\ 0.000 & 9.375\times10^{-1} & 1.230 & 5.537 & 1.015\times10^{1} & 0.000 & -1.856\times10^{2} \\ -9.375\times10^{-1} & 8.203\times10^{-1} & 5.537 & 1.015\times10^{1} & 6.598\times10^{1} & 1.856\times10^{2} & 2.629\times10^{2} \\ -4.10156 & -1.8457 & 1.015\times10^{1} & 6.598\times10^{1} & 1.547\times10^{2} & 1.315\times10^{3} & 4.995\times10^{3} \\ -1.661\times10^{1} & -2.030\times10^{1} & 0.000 & 1.856\times10^{2} & 1.315\times10^{3} & 3.746\times10^{3} & 3.934\times10^{4} \\ -7.106\times10^{1} & -1.320\times10^{2} & -1.856\times10^{2} & 2.629\times10^{2} & 4.995\times10^{3} & 3.934\times10^{4} & 1.319\times10^{5} \end{pmatrix}$$

The matrix elements $M^{3,n_1,n_2,0,0}_{0,1,1}$ for $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ divided by $M^{2,1,1,0,0}_{0,1,1}$ are given as

$$\begin{pmatrix} -2.143\times10^{-1} & 1.107 & 4.286\times10^{-1} & -2.009\times10^{-1} & -2.804 & -1.534\times10^{1} & -7.890\times10^{1} \\ 1.107 & 3.125\times10^{-1} & 8.438\times10^{-1} & 1.364 & 1.421 & -6.724 & -83.39\times10^{1} \\ 4.286\times10^{-1} & 8.438\times10^{-1} & 8.412\times10^{-1} & 4.175 & 1.127\times10^{1} & 2.610\times10^{1} & -2.651 \\ -2.009\times10^{-1} & 1.364 & 4.175 & 6.526 & 4.604\times10^{1} & 1.723\times10^{2} & 5.998\times10^{2} \\ -2.804 & 1.421 & 1.127\times10^{1} & 4.604\times10^{1} & 9.647\times10^{1} & 8.782\times10^{2} & 4.188\times10^{3} \\ -1.534\times10^{1} & -6.724 & 2.610\times10^{1} & 1.723\times10^{2} & 8.782\times10^{2} & 2.296\times10^{3} & 2.556\times10^{4} \\ -7.890\times10^{1} & -8.339\times10^{1} & -2.651 & 5.998\times10^{2} & 4.188\times10^{3} & 2.556\times10^{4} & 7.990\times10^{4} \end{pmatrix}$$

The matrix elements $M^{4,n_1,n_2,0,0}_{0,1,1}$ for $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ divided by $M^{2,1,1,0,0}_{0,1,1}$ are given as

$$\begin{pmatrix} -9.921\times10^{-3} & -1.994\times10^{-1} & 7.381\times10^{-1} & 3.679\times10^{-1} & -4.429\times10^{-1} & -5.552 & -3.669\times10^{1} \\ -1.994\times10^{-1} & 2.344\times10^{-1} & 4.297\times10^{-1} & 7.939\times10^{-1} & 1.640 & 1.920 & -1.535\times10^{1} \\ 7.381\times10^{-1} & 4.297\times10^{-1} & 3.472\times10^{-1} & 1.709 & 5.241 & 1.727\times10^{1} & 4.837\times10^{1} \\ 3.679\times10^{-1} & 7.939\times10^{-1} & 1.709 & 2.458 & 1.759\times10^{1} & 7.272\times10^{1} & 3.209\times10^{2} \\ -4.429\times10^{-1} & 1.640 & 5.241 & 1.759\times10^{1} & 3.502\times10^{1} & 3.241\times10^{2} & 1.675\times10^{3} \\ -5.552 & 1.920 & 1.727\times10^{1} & 7.272\times10^{1} & 3.241\times10^{2} & 8.171\times10^{2} & 9.241\times10^{3} \\ -3.669\times10^{1} & -1.535\times10^{1} & 4.837\times10^{1} & 3.209\times10^{2} & 1.675\times10^{3} & 9.241\times10^{3} & 2.809\times10^{4} \end{pmatrix}$$

The matrix elements $M^{5,n_1,n_2,0,0}_{0,1,1}$ for $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ divided by $M^{2,1,1,0,0}_{0,1,1}$ are given as

$$\begin{pmatrix} -6.313\times10^{-4} & -8.342\times10^{-3} & -1.088\times10^{-1} & 5.386\times10^{-1} & 3.223\times10^{-1} & -6.974\times10^{-1} & -9.148 \\ -8.342\times10^{-3} & -3.906\times10^{-2} & 2.539\times10^{-1} & 3.149\times10^{-1} & 7.379\times10^{-1} & 1.853 & 2.361 \\ -1.088\times10^{-1} & 2.539\times10^{-1} & 1.209\times10^{-1} & 5.284\times10^{-1} & 1.632 & 6.046 & 2.361\times10^{1} \\ 5.386\times10^{-1} & 3.149\times10^{-1} & 5.284\times10^{-1} & 6.993\times10^{-1} & 4.906 & 2.087\times10^{1} & 1.008\times10^{2} \\ 3.223\times10^{-1} & 7.379\times10^{-1} & 1.632 & 4.906 & 9.396 & 8.670\times10^{1} & 4.612\times10^{2} \\ -6.974\times10^{-1} & 1.853 & 6.046 & 2.087\times10^{1} & 8.670\times10^{1} & 2.133\times10^{2} & 2.417\times10^{3} \\ -9.148 & 2.361 & 2.361\times10^{1} & 1.008\times10^{2} & 4.612\times10^{2} & 2.417\times10^{3} & 7.216\times10^{3} \end{pmatrix}$$

The matrix elements $M_{0,1,1}^{6,n_1,n_2,0,0}$ for $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ divided by $M_{0,1,1}^{2,1,1,0,0}$ are given as

$$\begin{pmatrix} -3.902\times10^{-5} & -4.947\times10^{-4} & -3.850\times10^{-3} & -6.637\times10^{-2} & 4.158\times10^{-1} & 2.872\times10^{-1} & -9.554\times10^{-1} \\ -4.947\times10^{-4} & -1.628\times10^{-3} & -3.662\times10^{-2} & 1.559\times10^{-1} & 2.430\times10^{-1} & 6.887\times10^{-1} & 2.033 \\ -3.850\times10^{-3} & -3.662\times10^{-2} & 5.814\times10^{-2} & 1.499\times10^{-1} & 4.137\times10^{-1} & 1.542\times10^{-1} & 6.713 \\ -6.637\times10^{-2} & 1.559\times10^{-1} & 1.499\times10^{-1} & 1.698\times10^{-1} & 1.124 & 4.730 & 2.351\times10^{1} \\ 4.158\times10^{-1} & 2.430\times10^{-1} & 4.137\times10^{-1} & 1.124 & 2.055 & 1.864\times10^{1} & 9.971\times10^{1} \\ 2.872\times10^{-1} & 6.887\times10^{-1} & 1.542 & 4.730 & 1.864\times10^{1} & 4.477\times10^{1} & 5.042\times10^{2} \\ -9.554\times10^{-1} & 2.033 & 6.713 & 2.351\times10^{1} & 9.971\times10^{1} & 5.042\times10^{2} & 1.483\times10^{3} \end{pmatrix}$$

F.3 $M_{2,2,0}^{r,n_1,0,0,0}$ for $0 \leq r \leq 6$ and $0 \leq n_1 \leq 6$, and $M_{2,1,1}^{r,n_1,n_2,0,0}$ for $0 \leq r \leq 6$, $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$

The matrix elements $M_{2,2,0}^{r,n_1,0,0,0}$ for $0 \leq r \leq 6$ and $0 \leq n_1 \leq 6$ divided by $M_{2,2,0}^{0,0,0,0,0} = -\frac{8}{5}\left(\frac{m}{2\kappa T}\right)^{-\frac{1}{2}}\sqrt{2\pi}n^2\sigma^2$ calculated from eq.(E.9) are given as

$$\begin{pmatrix} 1 & -2.500\times10^{-1} & -6.250\times10^{-2} & -4.688\times10^{-2} & -5.859\times10^{-2} & -1.025\times10^{-1} & -2.307\times10^{-1} \\ -7.143\times10^{-2} & 1.220 & -7.277\times10^{-1} & -3.203\times10^{-1} & -3.686\times10^{-1} & -6.519\times10^{-1} & -1.529 \\ -1.984\times10^{-3} & -8.085\times10^{-2} & 1.474 & -1.399 & -8.883\times10^{-1} & -1.385 & -3.177 \\ -9.019\times10^{-5} & -2.157\times10^{-3} & -8.479\times10^{-2} & 1.720 & -2.228 & -1.847 & -3.629 \\ -4.336\times10^{-6} & -9.546\times10^{-5} & -2.071\times10^{-3} & -8.568\times10^{-2} & 1.950 & -3.190 & -3.263 \\ -2.023\times10^{-7} & -4.502\times10^{-6} & -8.606\times10^{-5} & -1.894\times10^{-3} & -8.508\times10^{-2} & 2.164 & -4.272 \\ -8.927\times10^{-9} & -2.071\times10^{-7} & -3.872\times10^{-6} & -7.299\times10^{-5} & -1.706\times10^{-3} & -8.376\times10^{-2} & 2.364 \end{pmatrix}$$

The matrix elements $M_{2,1,1}^{0,n_1,n_2,0,0}$ for $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ divided by $M_{2,1,1}^{0,1,1,0,0} = \frac{1}{30}\left(\frac{m}{2\kappa T}\right)^{-\frac{1}{2}}\sqrt{2\pi}n^2\sigma^2$ calculated from eq.(E.10) are given as

$$\begin{pmatrix} 1 & 1.500 & 1.875 & 3.281 & 7.383 & 2.030\times10^{1} & 6.598\times10^{1} \\ 1.500 & 9.375\times10^{-1} & 3.281 & 7.383 & 2.030\times10^{1} & 6.598\times10^{1} & 2.474\times10^{2} \\ 1.875 & 3.281 & 3.691 & 2.030\times10^{1} & 6.598\times10^{1} & 2.474\times10^{2} & 1.052\times10^{3} \\ 3.281 & 7.383 & 2.030\times10^{1} & 3.299\times10^{1} & 2.474\times10^{2} & 1.052\times10^{3} & 4.995\times10^{3} \\ 7.383 & 2.030\times10^{1} & 6.598\times10^{1} & 2.474\times10^{2} & 5.258\times10^{2} & 4.995\times10^{3} & 2.622\times10^{4} \\ 2.030\times10^{1} & 6.598\times10^{1} & 2.474\times10^{2} & 1.052\times10^{3} & 4.995\times10^{3} & 1.311\times10^{4} & 1.508\times10^{5} \\ 6.598\times10^{1} & 2.474\times10^{2} & 1.052\times10^{3} & 4.995\times10^{3} & 2.622\times10^{4} & 1.508\times10^{5} & 4.712\times10^{5} \end{pmatrix}$$

The matrix elements $M_{2,1,1}^{1,n_1,n_2,0,0}$ for $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ divided by $M_{2,1,1}^{0,1,1,0,0}$ are given as

$$\begin{pmatrix} 2.119 & 2.060 & 3.080 & 6.752 & 1.861 \times 10^1 & 6.104 \times 10^1 & 2.312 \times 10^2 \\ 2.060 & 7.545 \times 10^{-1} & 2.824 & 8.301 & 3.010 \times 10^1 & 1.248 \times 10^2 & 5.770 \times 10^2 \\ 3.080 & 2.824 & 2.432 & 1.463 \times 10^1 & 6.103 \times 10^1 & 3.005 \times 10^2 & 7.988 \times 10^2 \\ 6.752 & 8.301 & 1.463 \times 10^1 & 1.988 \times 10^1 & 1.622 \times 10^2 & 8.616 \times 10^2 & 2.230 \times 10^3 \\ 1.861 \times 10^1 & 3.010 \times 10^1 & 6.103 \times 10^1 & 1.622 \times 10^2 & 3.012 \times 10^2 & 3.086 \times 10^3 & 8.499 \times 10^3 \\ 6.104 \times 10^1 & 1.248 \times 10^2 & 3.005 \times 10^2 & 8.616 \times 10^2 & 3.086 \times 10^3 & 7.270 \times 10^3 & 4.187 \times 10^4 \\ 2.312 \times 10^2 & 5.770 \times 10^2 & 1.639 \times 10^3 & 5.289 \times 10^3 & 1.977 \times 10^4 & 8.945 \times 10^4 & 1.235 \times 10^5 \end{pmatrix}$$

The matrix elements $M_{2,1,1}^{2,n_1,n_2,0,0}$ for $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ divided by $M_{2,1,1}^{0,1,1,0,0}$ are given as

$$\begin{pmatrix} -3.208 & 3.723 & 2.353 & 4.680 & 1.408 \times 10^1 & 5.246 \times 10^1 & 2.261 \times 10^2 \\ 3.723 & 7.839 \times 10^{-1} & 1.930 & 4.372 & 1.543 \times 10^1 & 7.100 \times 10^1 & 3.800 \times 10^2 \\ 2.353 & 1.930 & 1.639 & 8.168 & 2.855 \times 10^1 & 1.354 \times 10^2 & 7.988 \times 10^2 \\ 4.680 & 4.372 & 8.168 & 1.142 \times 10^1 & 8.268 \times 10^1 & 3.816 \times 10^2 & 2.230 \times 10^3 \\ 1.408 \times 10^1 & 1.543 \times 10^1 & 2.855 \times 10^1 & 8.268 \times 10^1 & 1.590 \times 10^2 & 1.494 \times 10^3 & 8.499 \times 10^3 \\ 5.246 \times 10^1 & 7.100 \times 10^1 & 1.354 \times 10^2 & 3.816 \times 10^2 & 1.494 \times 10^3 & 3.642 \times 10^3 & 4.187 \times 10^4 \\ 2.261 \times 10^2 & 3.800 \times 10^2 & 7.988 \times 10^2 & 2.230 \times 10^3 & 8.499 \times 10^3 & 4.187 \times 10^4 & 1.2345 \times 10^5 \end{pmatrix}$$

The matrix elements $M_{2,1,1}^{3,n_1,n_2,0,0}$ for $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ divided by $M_{2,1,1}^{0,1,1,0,0}$ are given as

$$\begin{pmatrix} 2.316 \times 10^{-1} & -3.556 & 2.962 & 2.416 & 6.145 & 2.369 \times 10^1 & 1.115 \times 10^2 \\ -3.556 & 1.270 & 1.419 & 2.159 & 5.757 & 2.388 \times 10^1 & 1.323 \times 10^2 \\ 2.962 & 1.419 & 9.495 \times 10^{-1} & 4.013 & 1.170 \times 10^1 & 4.614 \times 10^1 & 2.451 \times 10^2 \\ 2.416 & 2.159 & 4.013 & 5.255 & 3.507 \times 10^1 & 1.441 \times 10^2 & 7.320 \times 10^2 \\ 6.145 & 5.757 & 1.170 \times 10^1 & 3.507 \times 10^1 & 6.573 \times 10^1 & 5.863 \times 10^2 & 3.063 \times 10^3 \\ 2.369 \times 10^1 & 2.388 \times 10^1 & 4.614 \times 10^1 & 1.441 \times 10^2 & 5.863 \times 10^2 & 1.414 \times 10^3 & 1.566 \times 10^4 \\ 1.115 \times 10^2 & 1.323 \times 10^2 & 2.451 \times 10^2 & 7.320 \times 10^2 & 3.063 \times 10^3 & 1.566 \times 10^4 & 4.598 \times 10^4 \end{pmatrix}$$

The matrix elements $M_{2,1,1}^{4,n_1,n_2,0,0}$ for $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ divided by $M_{2,1,1}^{0,1,1,0,0}$ are given as

$$\begin{pmatrix} 6.619 \times 10^{-3} & 2.151 \times 10^{-1} & -2.217 & 2.385 & 2.398 & 7.504 & 3.549 \times 10^1 \\ 2.151 \times 10^{-1} & -8.309 \times 10^{-1} & 1.685 & 1.211 & 2.238 & 6.959 & 3.336 \times 10^1 \\ -2.217 & 1.685 & 5.252 \times 10^{-1} & 1.737 & 4.391 & 1.488 \times 10^1 & 6.628 \times 10^1 \\ 2.385 & 1.211 & 1.737 & 1.982 & 1.219 \times 10^1 & 4.681 \times 10^1 & 2.172 \times 10^2 \\ 2.398 & 2.238 & 4.391 & 1.219 \times 10^1 & 2.157 \times 10^1 & 1.843 \times 10^2 & 9.230 \times 10^2 \\ 7.504 & 6.959 & 1.488 \times 10^1 & 4.681 \times 10^1 & 1.843 \times 10^2 & 4.308 \times 10^2 & 4.644 \times 10^3 \\ 3.549 \times 10^1 & 3.336 \times 10^1 & 6.628 \times 10^1 & 2.172 \times 10^2 & 9.230 \times 10^2 & 4.644 \times 10^3 & 1.337 \times 10^4 \end{pmatrix}$$

The matrix elements $M_{2,1,1}^{5,n_1,n_2,0,0}$ for $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ divided by $M_{2,1,1}^{0,1,1,0,0}$ are given as

$$\begin{pmatrix}
3.0725\times10^{-4} & 5.543\times10^{-3} & 1.139\times10^{-1} & -1.491 & 1.962 & 2.350 & 8.783 \\
5.543\times10^{-3} & 4.365\times10^{-2} & -8.964\times10^{-1} & 1.169 & 1.029 & 2.246 & 8.021 \\
1.139\times10^{-1} & -8.964\times10^{-1} & 4.822\times10^{-1} & 7.664\times10^{-1} & 1.534 & 4.554 & 1.770\times10^{1} \\
-1.491 & 1.169 & 7.664\times10^{-1} & 6.762\times10^{-1} & 3.673 & 1.312\times10^{1} & 5.745\times10^{1} \\
1.962 & 1.029 & 1.534 & 3.673 & 5.965 & 4.841\times10^{1} & 2.340\times10^{2} \\
2.350 & 2.246 & 4.554 & 1.312\times10^{1} & 4.841\times10^{1} & 1.083\times10^{2} & 1.135\times10^{3} \\
8.783 & 8.021 & 1.770\times10^{1} & 5.745\times10^{1} & 2.340\times10^{2} & 1.135\times10^{3} & 3.182\times10^{3}
\end{pmatrix}$$

The matrix elements $M_{2,1,1}^{6,n_1,n_2,0,0}$ for $1 \leq n_1 \leq 7$ and $1 \leq n_2 \leq 7$ divided by $M_{2,1,1}^{0,1,1,0,0}$ are given as

$$\begin{pmatrix}
1.499\times10^{-5} & 2.398\times10^{-4} & 2.580\times10^{-3} & 6.649\times10^{-2} & -1.060 & 1.646 & 2.293 \\
2.398\times10^{-4} & 1.062\times10^{-3} & 4.099\times10^{-2} & -5.314\times10^{-1} & 8.456\times10^{-1} & 8.811\times10^{-1} & 2.222 \\
2.580\times10^{-3} & 4.099\times10^{-2} & -2.132\times10^{-1} & 5.888\times10^{-1} & 5.703\times10^{-1} & 1.346 & 4.602 \\
6.649\times10^{-2} & -5.314\times10^{-1} & 5.888\times10^{-1} & 2.452\times10^{-1} & 1.044 & 3.317 & 1.358\times10^{1} \\
-1.060 & 8.456\times10^{-1} & 5.703\times10^{-1} & 1.044 & 1.483 & 1.115\times10^{1} & 5.149\times10^{1} \\
1.646 & 8.811\times10^{-1} & 1.346 & 3.317 & 1.115\times10^{1} & 2.355\times10^{1} & 2.379\times10^{2} \\
2.293 & 2.222 & 4.602 & 1.358\times10^{1} & 5.149\times10^{1} & 2.379\times10^{2} & 6.454\times10^{2}
\end{pmatrix}$$

Bibliography

[1] S. Chapman and T. G. Cowling. *The Mathematical Theory of Non-uniform Gases (3rd edition).* Cambridge University Press, 1970.

[2] J. A. Mclennan. *Introduction to Nonequilibrium Statistical Mechanics.* Prentice Hall,Englewood Cliffs, 1989.

[3] P. Résibois and M. De Leener. *Classical Kinetic Theory of Fluids.* A Wiley-Interscience Publication, 1977.

[4] M. N. Kogan. *Rarefied Gas Dynamics.* Plenum Press, 1969.

[5] C. Cercignani. *Mathematical Methods in Kinetic Theory.* Plenum Press, 1990.

[6] S. Flügge. *Thermodynamics of Gases.* Springer-Verlag, 1958.

[7] Y. Sone. *Kinetic Theory and Fluid Dynamics.* Birkhäuser, 2002.

[8] B. C. Eu. *Nonequilibrium Statistical Mechanics.* Kluwer Academic Press, 1998.

[9] D. Enskog. *Kinetische Theorie der Vorgänge in mässig verdünten Gases.* Almqvist and Wiksells, 1917.

[10] K. A. Fiscko, D. P. Weaver D. R. Chapman, ed. E. P. Muntz, and D.H. Campbell. *Rarefied Gas Dynamics Mechanics of Nonequilibrium Processes.* American Institute of Aeronautics and Astronautics, 1989.

[11] C. S. Wang-Chang, ed. J. de Boer G. E. Uhlenbeck, and G. E. Uhlenbeck. *Studies in Statistical Mechanics*, volume V. North-Holland, 1970.

[12] J. H. Ferziger and H. G. Kaper. *Mathematical Theory of Transport Processes in Gases.* North-Holland Publishing Company, 1972.

[13] J. L. Lebowitz and E. W. Montroll. *The Boltzmann equation.* Elsevier Science, 1983.

[14] E. G. D. Cohen and W. Thirring. *The Boltzmann equation : theory and applications.* Springer-Verlag, 1973.

[15] C. Cercignani. *The Boltzmann equation and its applications.* Springer-Verlag, 1988.

[16] C. Cercignani. *Theory and application of the Boltzmann equation.* Chatto and Windus, 1975.

[17] V. V. Aristov. *Direct Method for Solving the Boltzmann equation and Study of Nonequilibrium Flows.* Kluwer Academic Publishers, 2001.

[18] R. D. Present. *Kinetic Theory of Gases.* Mcgraw-Hill, 1958.

[19] P.P.J.M. Schram. *Kinetic theory of gases and plasmas.* Kluwer Academic Pubication, 1991.

[20] D.C. Montgomery and D.A. Tidman. *Plasma kinetic theory.* McGraw-Hill, 1964.

[21] W. E. Köhler F. R. W. McCourt, J. J. M. Beenakker and I. Kuščer. *Nonequilibrium Phenomena in Polyatomic Gases.* Clarendon Press, 1990.

[22] J. C. Maxwell. *Collected papers*, 2:42, 1890.

[23] J. C. Maxwell. *Phil. Trans. R. Soc.*, 157:49, 1867.

[24] E. Ikenberry and C. Truesdell. *J. Rational Mech. Anal.*, 5:1, 1956.

[25] D. Burnett. *Proc. Lond. Math. Soc.*, 40:382, 1935.

[26] R. Schamberg. *Ph. D thesis, California Institute of Technology*, 1947.

[27] M. Sh. Shavaliev. *J. Appl. Math. Mech.*, 42:698, 1978.

[28] N. K. Makashev E. S. Asmolov and V. I. Nosik. *Sov. Phys. Dokl.*, 24:892, 1979.

[29] Y. Pomeau and P. Résibois. *Phys. Rep.*, 19:63, 1975.

[30] L. E. Reichl. *A Modern Course in Statistical Physics (2nd edition).* University of Texas Press, 1998.

[31] T. R. Kirkpatrick J. R. Dorfman and J. V. Sengers. *Annu. Rev. Phys. Chem.*, 45:213, 1994.

[32] M. Fushiki. *private communication, in preparation.*

[33] V. Morozov D. Zubarev and G. Ropke. *Statistical Mechanics of Nonequilibrium Processes I, II.* Akademie Verlag, 1996.

[34] W. W. Wood. *Acta Phys. Aust. Suppl.*, X:451, 1973.

[35] B. J. Alder and T. E. Wainwright. *Phys. Rev. A*, 1:18, 1970.

[36] J. R. Dorfman and E. G. D. Cohen. *Phys. Rev. Lett.*, 25:1257, 1970.

[37] S. Yukawa T. Murakami, T. Shimada and N. Ito. *J. Phys. Soc. Jpn.*, 72:1049, 2003.

[38] M. H. Ernst and J. R. Dorfman. *Physica*, 61:157, 1972.

[39] J. A. Mclennan. *Phys. Rev. A*, 8:1479, 1973.

[40] J. W. Dufty and J. A. Mclennan. *Phys. Rev. A*, 9:1266, 1974.

[41] C. Eckart. *Phys. Rev.*, 58:267, 1940.

[42] C. Eckart. *Phys. Rev.*, 58:269, 1940.

[43] C. Eckart. *Phys. Rev.*, 58:919, 1957.

[44] M. B. Romero and R. M. Velasco. *Physica A*, 222:161, 1995.

[45] H. Grad. *Comm. Pure Appl. Math.*, 2:331, 1949.

[46] S. Reinecke and G. M. Kremer. *Continuum Mech. Thermodyn.*, 3:155, 1991.

[47] S. Reinecke and G. M. Kremer. *Continuum Mech. Thermodyn.*, 8:121, 1996.

[48] I. V. Karlin and A. N. Gorban. *Annalen der Physik*, 11:783, 2002.

[49] S. Chapman. *Phylos. Trans. Roy. Soc. London*, 216:279, 1916.

[50] S. Chapman. *Proc. Roy. Soc. London*, A 93:1, 1916.

[51] D. Hilbert. *Math. Annalen*, 72:567, 1912.

[52] D. Hilbert. *Grundzüge einer Allgemeinen Theorie der Linearen Integralgleichungen Chapter 22.* Teubner, 1912.

[53] L. S. García-Colín F. J. Uribe, R. M. Velasco and E. Díaz-Herreera. *Phys. Rev. E*, 62:6649, 2000.

[54] E. Salomons and M. Mareschal. *Phys. Rev. Lett.*, 69:269, 1992.

[55] H. Rao X. Chen and E. A. Spiegel. *Phys. Rev. E*, 64:046309, 2001.

[56] M. Al-Ghoul and B. C. Eu. *Phys. Rev. E*, 64:046303, 2001.

[57] L. H. Thomas. *J. Chem. Phys.*, 12:449, 1944.

[58] J. D. Foch Jr. *Acta Phys. Aust. Suppl.*, X:123, 1973.

[59] Kim H.-D. and H. Hayakawa. *J. Phys. Soc. Jpn.*, 72:1904, 2003.

[60] J. Fort and A. S. Cukrowski. *Chem. Phys.*, 222:59, 1997.

[61] C. Cercignani. *University of California Report*, No. AS-64-19, 1964.

[62] E. P. Gross P. L. Bhatnagar and M. Krook. *Phys. Rev.*, 94:511, 1954.

[63] J. L. Lebowitz. *Phys. Rev.*, 114:1192, 1959.

[64] Y. J. Park and C. S. Kim. *J. Korean Phys. Soc.*, 29:466, 1996.

[65] F. Bouchut and B. Perthame. *J. Stat. Phys.*, 71:191, 1993.

[66] C. S. Kim A. Santos, J. J. Brey and J. W. Dufty. *Phys. Rev. A*, 39:320, 1989.

[67] A. Santos C. S. Kim, J. W. Dufty and J. J. Brey. *Phys. Rev. A*, 39:328, 1989.

[68] A. Santos C. S. Kim, J. W. Dufty and J. J. Brey. *Phys. Rev. A*, 40:7165, 1989.

[69] A. Santos and J. J. Brey. *Physica A*, 174:355, 1991.

[70] A. Santos J. J. Brey and J. W. Dufty. *Phys. Rev. A*, 36:2842, 1987.

[71] M. Tij and A. Santos. *Phys. Fluids*, 7:2858, 1995.

[72] J. M. Montanero and A. Santos. *Physica A*, 225:7, 1996.

[73] A. Santos. *Phys. Rev. E*, 62:6597, 2000.

[74] L. Trilling. *Phys. Fluid*, 7:1681, 1964.

[75] R. K. Agarwal R. Balakrishnan and K.-Y. Yun. *J. Therm. Heat Trans.*, 13:397, 1999.

[76] Kim H.-D. and H. Hayakawa. *J. Phys. Soc. Jpn.*, 70:1954, 2001.

[77] T.P.C. van Noije and M.H. Ernst. *Granular Matter*, 1:57, 1998.

[78] S.E. Esipov and T. Pöschel. *J. Stat. Phys.*, 86:1997, 1385.

[79] M.J. Ruiz-Montero J. J. Brey and D.Cubero. *Phys. Rev. E*, 54:3664, 1996.

[80] D. Cubero J. J. Brey and M.J. Ruiz-Montero. *Phys. Rev. E*, 59:1256, 1999.

[81] N. V. Brilliantov and T. Pöschel. *Phys. Rev. E*, 61:2809, 2000.

[82] D.R. Wilkinson and S.F. Edwards. *Proc. R. Soc. Lond. A*, 381:33, 1982.

[83] P. A. Martin and J. Piasecki. *Physica A*, 265:19, 1999.

[84] W.-K. Lu D. W. Condiff and J. S. Dahler. *J. Chem. Phys.*, 42:3445, 1965.

[85] C. F. Curtiss. *J. Chem. Phys.*, 24:225, 1956.

[86] G. M. Kremer. *Continuum Mech. Thermodyn.*, 9:13, 1997.

[87] I. Prigogine and E. Xhrouet. *Physica*, 15:913, 1949.

[88] R. D. Present. *J. Chem. Phys.*, 31:747, 1959.

[89] R. D. Present. *Proc. Natl. Acad. Sci. USA*, 41:415, 1955.

[90] B. Schizgal and M. Karplus. *J. Chem. Phys.*, 52:4262, 1970.

[91] W. Stiller A. S. Cukrowski and R. Schmidt. *Theor. Chim. Acta*, 73:67, 1988.

[92] M. A. Eliason and J. O. Hirschfelder. *J. Chem. Phys.*, 30:1426, 1959.

[93] R. D. Levine and R. B. Bernstein. *Molecular Reaction Dynamics and Chemical Reactivity*. Oxford University Press, 1987.

[94] C. W. Pyun and J. Ross. *J. Chem. Phys.*, 40:2572, 1964.

[95] B. Schizgal. *J. Chem. Phys.*, 55:76, 1971.

[96] S. Hudson R. Kapral and J. Ross. *J. Chem. Phys.*, 53:4387, 1970.

[97] A. S. Cukrowski and J. Popielawski. *Acta Phys. Pol. A*, 70:321, 1986.

[98] J. Popielawski. *J. Chem. Phys.*, 83:790, 1985.

[99] A. S. Cukrowski J. Popielawski and S. Fritzsche. *Physica A*, 188:344, 1992.

[100] J. Fort and A. S. Cukrowski. *Acta Phys. Polo. B*, 29:1633, 1998.

[101] A. S. Cukrowski and J. Popielawski. *Chem. Phys.*, 109:215, 1986.

[102] B. C. Eu and K.-W. Li. *Physica*, 88A:135, 1977.

[103] D. G. Napier and B. D. Shizgal. *Phys. Rev. E*, 52:3797, 1995.

[104] B. D. Shizgal and D. G. Napier. *Physica A*, 223:50, 1996.

[105] S. Fritzsche A. S. Cukrowski and J. Fort. *Chem. Phys. Lett.*, 341:585, 2001.

[106] J. Fort A. S. Cukrowski and S. Fritzsche. *Acta Phys. Pol. B*, 33:1085, 2002.

[107] B. C. Eu. *J. Chem. Phys.*, 108:5834, 1998.

[108] R. E. Nettleton. *Z. Phys. Chem.*, 196:177, 1996.

[109] R. E. Nettleton. *J. Phys. Chem.*, 100:11005, 1996.

[110] J. Casas-Vázquez D. Jou and G. Lebon. *Extended Irreversible Thermodynamics 3rd edition.* Springer, 2001.

[111] J. Casas-Vázquez D. Jou and G. Lebon. *Rep. Prog. Phys.*, 62:1035, 1999.

[112] J. Casas-Vázquez D. Jou and G. Lebon. *J. Non-Equilib. Thermodyn.*, 23:277, 1998.

[113] C. E. Shannon and W. Weaver. *The Mathematical Theory of Communication.* University of Illinois Press, 1949.

[114] L. Brillouin. *Science and Information Theory 2nd edition.* Academic, 1962.

[115] E. T. Jaynes. *Phys. Rev.*, 106:620, 1957.

[116] D. Zubarev. *Dokl. Akad. Nauk SSSR, Ser. Fiz.*, 140:92, 1961.

[117] A. Katz. *Principles of Statistical Mechanics.* Freeman, 1967.

[118] D. Jou and M. Criado-Sancho. *Physica A*, 292:75, 2001.

[119] R. Dominguez and D. Jou. *Phys. Rev. E*, 51:158, 1995.

[120] J. Casas-Vázquez and D.Jou. *Phys. Rev. E*, 49:1040, 1994.

[121] J. Camacho and D. Jou. *Phys. Rev. E*, 52:3490, 1995.

[122] M. S. Mongiovì. *Phys. Rev. E*, 63:061202, 2001.

[123] R. Dominguez-Cascante and J. Faraudo. *Phys. Rev. E*, 54:6933, 1996.

[124] J. Fort. *Phys. Rev. E*, 59:3710, 1999.

[125] D. Jou J. Fort and J. E. Llebot. *Physica A*, 248:97, 1998.

[126] D. Jou J. Fort and J. E. Llebot. *Physica A*, 269:439, 1999.

[127] J. Fort and J. E. Llebot. *J. Math. Phys.*, 39:345, 1998.

[128] R. E. Nettleton. *J. Chem. Phys.*, 106:10311, 1997.

[129] R. E. Nettleton. *Phys. Rev. E*, 53:1241, 1996.

[130] Kim H.-D. and H. Hayakawa. *Chem. Phys. Lett.*, 372:314, 2003.

[131] I. Prigogine. *Etude thermodynamique des phénomènes irréversibles*. Dunod, 1947.

[132] S. R. de Groot and P. Mazur. *Nonequilibrium Thermodynamics*. North-Holland, 1963.

[133] I. Mëller and T. Ruggeri. *Extended Thermodynamics*. Springer-Verlag, 1993.

[134] D. Reitebuch I. Mëller and W. Weiss. *Continuum Mech. Thermodyn.*, 15:113, 2002.

[135] M. A. Rincon I. Liu and I. Mëller. *Continuum Mech. Thermodyn.*, 14:483, 2002.

[136] M. S. Mongiovì. *Math. Comp. Model.*, 36:951, 2002.

[137] J. Casas-Vázquez J. Fort and V. Méndez. *J. Phys. Chem.*, B 103:860, 1999.

[138] S. Sasa and H. Tasaki. *http://xxx.yukawa.kyoto-u.ac.jp/abs/cond-mat/0108365*.

[139] Y. Oono and M. Paniconi. *Prog. Theor. Phys. Suppl.*, 130:29, 1998.

[140] *http://ace.phys.h.kyoto-u.ac.jp/~kim/supplement.html*.

[141] S. Chapman. *Mem. and Proc. Manchester Lit. and Phil. Soc.*, 66, 1922.

[142] G. Casati D. Alonso, R. Artuso and I. Guarneri. *Phys. Rev. Lett.*, 82:1859, 1999.

[143] R.W. MaC Cormack X.L. Zhang and D. R. Chapman. *AIAA journal*, 31:1036, 1993.

[144] M. Slemrod. *Physica D*, 109:257, 1997.

[145] A. V. Bobylev. *Sov. Phys. Dokl.*, 27:29, 1982.

[146] S. Succi. *The Lattice Boltzmann Equation.* Clarendon Press, 2001.

[147] Kim H.-D. and H. Hayakawa. *J. Phys. Soc. Jpn.*, 72:2473, 2003.

[148] Y. Sone and S. Takata. *Trans. Theor. Stat. Phys.*, 21:501, 1992.

[149] R. E. Nettleton. *Phys. Rev. E*, 54:2147, 1996.

[150] M. Casas A. R. Plastino and A. Plastino. *Physica A*, 280:289, 2000.

[151] Q. A. Wang. *Chaos, Solitons and Fractals*, 12:1431, 2001.

[152] J.-L. Barrat. *J. Phys.: Condens. Matter*, 15:S1, 2003.

[153] G. Sonnino A. L. Garcia and M. M. Mansour. *J. Stat. Phys.*, 90:1489, 1998.

[154] G. C. Lie M. M. Mansour, A. L. Garcia and E. Clementi. *Phys. Rev. Lett.*, 58:874, 1987.

[155] M. Abramowitz and I. A. Stegun. *Handbook of Mathematical Functions.* Dover Publications, 1970.